# Synthesis and Analytical Applications of Ion-Exchange Materials; Separation and Determination of Some Inorganic Ions.

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# S U M M A R Y

Detection of an ion can be achieved either by instrumental or by non-instrumental methods. The instrumental methods are sensitive and specific, but the non-instrumental methods are faster, simpler and sometimes they give more specific information than the instrumental techniques of the various non-instrumental methods. Spot tests are probably the most useful. These tests increase in elegance by the resin spot technique. The resin spot tests are very sensitive as the colour is concentrated on the small surface area of the resin bead. These tests are more selective also. If the resin bead is a cation exchanger than anion either do not interfere or they interfere only very slightly. Uptill now the resin spot tests have been concerned mainly with inorganic reactions.

Organic reactions are particularly amendable, to resin spot tests. The resins are efficient catalyst and once the catalysis is over they can be easily removed from the reaction medium. Now the change in pH if any due to the hydrolysis of the organic compound can be detected and this can lead to the detection of the parent organic substance. In this way excellent spot tests have been developed for esters, amides, imides and anilides. However, the possibilities have not been exhausted and more interes-

ting applications are possible.

The second problem in microanalysis is the rapid and selective determination of small quantities of materials. In this case if we wish to obtain accurate results we can not use a technique simpler than the spectrophotometry. This is probably the simplest and the most versatile method available for the purpose. Selectivity and sensitivity can be achieved by the use of an appropriate colour reaction. Since most colour reactions are available for cations, more spectrophotometric methods have been developed for cations than anions. Bromate is one of the anions for which many methods are not available. We have therefore developed a new colour reaction for bromate ions.

Of the various methods of separation ion-exchange is probably the most important. Ion exchangers may be organic or inorganic. In the last few years the inorganic ion exchangers have attracted considerable attention. These exchangers have been synthesized by a number of workers. Their properties depend upon the method of preparation, i.e., the pH of precipitation, the order of addition of reagents the concentration of the reagent etc. These exchangers differ from one another with respect to their chemical stability, their thermal stability and their selectivity. Therefore, it is necessary to compare the properties of these exchangers. This comparison will tell us the proper exchanger to be used in a particular situation.

The second Chapter describes the use of resin beads 'as

indicators in the redox and precipitation titrations'. Resin beads in Fe(III) form have been used in the titrations of Zn, Pb, Ag and Cd with potassium ferrocyanide. The colour changes from yellow to blue due to the formation of prussian blue on the resin surface. Addition of alcohol improves the results. Stannic arsenate beads in the Fe(III) form give better results as compared to the resin beads. Resin beads sorbed in diphenylamine have been used in the redox titrations. Fe(II) is titrated with potassium dichromate, ceric sulphate and potassium permanganate, and $Na_2S_2O_3$ is titrated with ceric sulphate after acidifying with sulphuric acid. Beads sorbed in p-dimethylaminobenzylidene rhodanene have been used in the titration of chloride, bromide and iodide with silver nitrate. Alcohol is also added in the case of chloride and bromide. On the resin surface a violet colour appears at the end point. This method has also been used for the titration of coloured solutions. The resin bead indicators have also been used for the simultaneous determination of Zn and Cl in $ZnCl_2$ solution and Pb(II) and in lead nitrate and silver nitrate mixtures using resin beads in Fe(III) and p-dimethylaminobenzylidene rhodanine forms respectively.

The third Chapter deals with the detection of nitriles by an ion-exchange method. The detection is based on two tests. In the first test, the test solution is heated with dilute sulphuric acid and a few Dowex 50 resin beads in the $H^+$ form. The resin beads are washed with distilled water and tested with Nessler's reagent. A red colour indicates a positive test.

In the second test the test solution is heated with a few resin beads in the $H^+$ form on a slow flame. The beads are washed with distilled water and then a drop of Nessler's reagent is added. A red colour on the resin surface indicates a positive test.

Nitriles give a positive response with test I and a negative response with test II. For unsubstituted amides and imides both the tests are positive. It is therefore possible to distinguish between amides and nitriles.

Alcohols, acids, hydrocarbons and their derivatives, aldehydes, ketones, carbohydrates, ethers esters, anilides, phenols, amines and heterocyclic bases do not give a positive test either for amides or nitriles.

The fourth Chapter deals with a comparative study of synthetic inorganic ion-exchangers based on titanium(IV). Five substances, i.e., titanium molybdate, titanium antimonate, titanium arsenate, titanium selenite and titanium tungstate have been prepared. Their ion-exchange capacity, composition chemical stability and thermal stability have been determined: Distribution coefficients of 26 metal ions in water, 0.01M and 0.1M nitric acid. 0.1M formic acid, 0.1M $NH_4NO_3$ and Acetone-nitric acid mixtures have also been estimated. Titanium tungstate is found to be most stable exchanger in nitric acid while titanium molybdate is the least stable. At higher temperature titanium antimonate shows considerable ion-exchange capacity. Titanium arsenate has the highest ion-exchange capacity. The following important separations have been developed

on these exchangers.

1. Cd from Hg(II) on titanium tungstate columns.
2. Ba from La on titanium arsenate.
3. Cu(II) from Pb(II) on titanium tungstate.
4. Zn from Pb(II) on titanium tungstate.

In order to investigate the effect of non-aqueous solvents on Kd values the following studies were made:

1. Kd values of 26 metal ions in Acetone on titanium antimonate exchanger.
2. Kd values of 26 metal ions in Acetone + 0.1M $HNO_3$ in 1:1, 1:9 on the titanium antimonate exchangers.
3. Kd values of 26 metal ions in Acetone + 0.1M $HNO_3$ (9:1) on titanium tungstate, titanium arsenate and titanium selenite exchangers.

In Chapter 5 a method for the determination of bromate ions with antipyrine has been described.

Procedure for determination of Bromate:

To 3 ml of 5% antipyrine solution are added 3 ml of 60% perchloric acid and, 1 ml of 0.1M sodium nitrile solution. Samples having a concentration range of 25.0 - 140.0 µg/ml of bromate ions are added. The solution is diluted to 10 ml with distilled water The absorbance is taken against the blank at 525 mµ.

Conformity with Beer's Law:

It is found that Beer's law is obeyed for solutions containing 25.0 - 140.0 μg/ml of bromate. Sensitivity as defined by Sandell was found to be 0.029 $BrO_3^-/cm^2$ for log Io/I = 0.04 with a molar absorptivity 2 x $10^3$ $mole^{-1}$ $cm^{-1}$ liter.

Effect of Diverse Ions in Bromate Determination:

It is found that 15 fold excess of the following ions caused no interference:

Al(III), Ba(II), Be(II), Bi(III), Cu(II), Cr(III), Ca(II), Co(II), Ga(III), Au(III), Hf(IV), In(III), Li(I), La(III), Pb(II), Mn(II), $Hg_2$(II), Ni(II), K(I), Na(I), Ag(I), Sr(II), Th(IV), Tl(I), Y(III), $NO_3^-$, $SO_4^{--}$, $I^-$ and $Br^-$.

The sixth Chapter summarized our studies on papers impregnated with stannic antimonate. 48 Metal ions have been chromatographed on these papers in nitric acid solutions of $10^{-4}$ to 4M concentrations. A new quantity Ri(Ri = Rf on untreated papers - Rf on treated papers) has been defined. Some important analytical separations on stannic antimonate papers have been achieved.

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# CHAPTER - I

## INTRODUCTION

Three problems are very important in micro-analysis:

(i) Simple methods for sensitive and specific detection.

(ii) Rapid techniques for selective determination.

(iii) Selective methods of separation.

Detection can be achieved either by using instrumental methodssuch as IR and UV spectroscopy or non-instrumental technique such as color reactionsand spot tests. The instrumental methods are very sensitive and specific but they are not so simple and rapid. The non-instrumental methods may not be as specific and sensitive as the instrumental ones but they have the definite advantage of being fast, simple and inexpensive. Such methods are ideally suited to Indian conditions where it is not easy to purchase and maintain an IR spectrophotometer in every College and University. Of the non-instrumental methods the most versatile are probably the spot tests first described systematically by Feigl[1]. These tests have been made more elegant by the resin spot technique proposed and developed by Yoffe[2] in 1953. These resin spot tests depend on the intense coloration of a few grains of a light colored ion-exchange resin

produced by the uptake from the reaction medium of ions having characteristic colors. These tests have the following advantages:

1. They are more sensitive because the colored ionic species is concentrated on the resin surface.

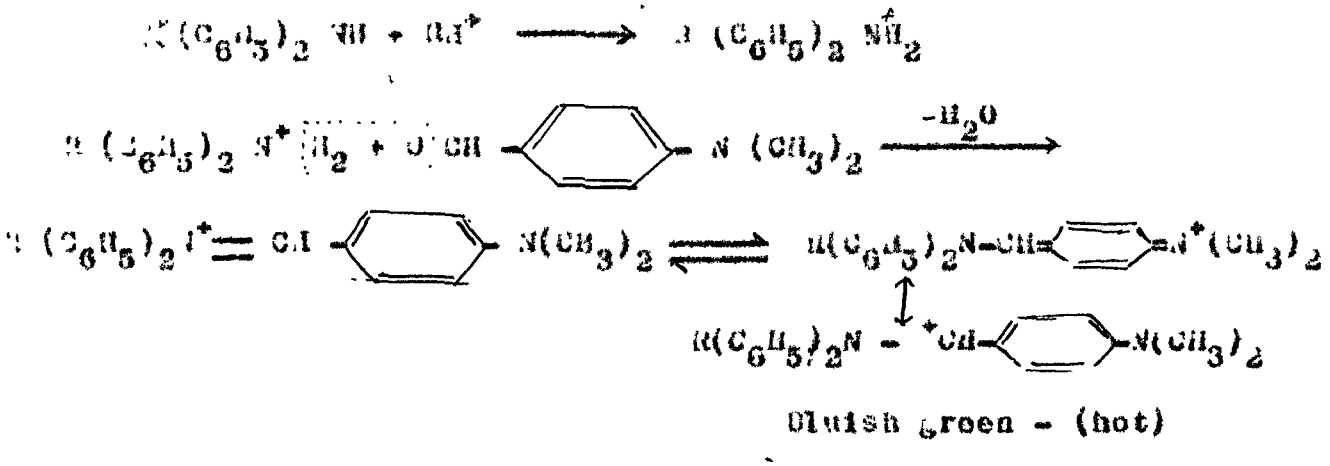
2. The coloration is often more stable in the resin phase than in the aqueous phase and sometimes becomes progressively more intense on standing.

3. These tests are more selective. Thus ions having a charge opposite to that of the ionic species adsorbed by the resin, usually do not interfere.

4. These tests need very little equipment and require very little training on the part of the investigator.

Most of the resin spot tests up-to-date have been used for the detection of inorganic ions by using color reaction already known[2,4,5]. Some tests have been described for the detection of phenols, aliphatic amines, primary aromatic amines, aldehydes and substituted hydrazines[6,7,8]. All these tests are resin spot modifications of already known color reactions. However, resin beads can also be used to develop new color reactions as was described by [illegible] uroni for diphenylamine[3]. In this test a few milligrams of the test substance in alcohol and a few resin beads are added to a microtest tube. One or two drops of p-dimethylaminobenzaldehyde solution are added. The contents are heated for 2 minutes. When diphenylamine is present a deep

yellow color appears on the resin beads at room temperature. This turns to green or bluish green on heating. The green color on the resin beads persists if the diphenylamine concentration is high, but it may vanish on cooling if the concentration is low. Even at low concentrations, however, the color reappears on the resin bead upon heating. Since the color is adsorbed on the resin beads, it is probably a positively charged compound which results from the condensation of $C_6H_5-NH_2^+ - C_6H_5$ with p-dimethylaminobenzaldehyde. The assumption is confirmed by the fact that a neutral solution of diphenylamine and p-dimethylaminobenzaldehyde do not react to give either a yellow or a green product. However, if hydrochloric acid is added, a yellow color is obtained which, on heating turns green or bluish green. The following mechanism has been postulated.




Another novel approach is to combine the hydrolysis and catalytic reactions of the resin beads with the resin spot technique. An interesting example of this approach is the detection of esters[10].

The principle of the method is simple. Ion exchangers hydrolyze esters more effectively than does an acid[11] and no new ions are introduced into the solution.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{HH^+} CH_3COOH + C_2H_5OH$$

The ion exchanger is easily removed from the solution by filtering through a glass wool plug. The consequent decrease in pH is readily detected with an indicator such as methyl red. A comparison of ion exchange method for the detection of esters has been made with the available classical methods[12,13]. The results are summarized in Table I.

TABLE - I

Comparison of the ion exchange method for the detection of esters with the Hydroxamic acid and enzymatic methods.

| Basis of comparison | Hydroxamic acid test | Enzymatic test | Ion-exchange test |
|---|---|---|---|
| Number of tests usually performed | Three tests are recommended | One test | One test |
| Effect of time | Best to note the color within 5 min. The color may diminish with time. | Note the color after 5 min. The color becomes more intense with time. | Color produced immediately. No effect of time. |
| Test with esters of inorganic acids. | Negative | Negative | Positive |
| Test with chloral hydrate. | Positive | Negative | Negative |

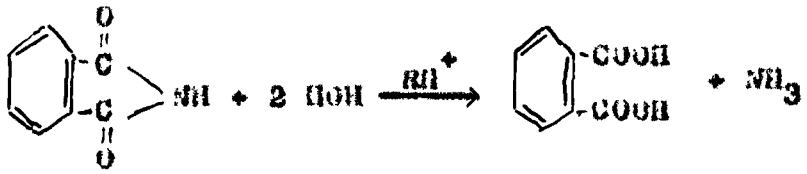
TABLE-I (Contd.)

| Basis of comparison | Hydroxamic acid test | Enzymatic test | Ion-exchange test |
|---|---|---|---|
| Test with chloroform | Positive | Negative | Negative |
| Test with formaldehyde and benzaldehyde | Weakly positive | Negative | Negative |
| Most amides | Positive | Negative | Positive |
| Acid esters | Weakly response | Weakly response | Definitely positive. |

The comparison shows that the resin spot technique offers definite advantages when compared with the classical methods.

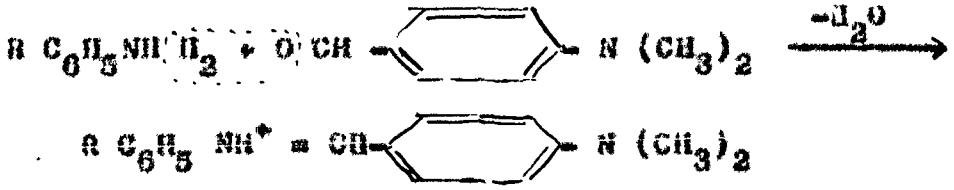
Another method in which the resin beads have been used for the catalytic hydrolysis and as the detection media, is the detection of amide, imide and anilides[14]. The hydrolysis of amides and imides is brought about by the $H^+$ form cation exchange resin which catalysis the acid hydrolysis to the corresponding acid and ammonia or aniline. Ammonia gas and aniline pick-up one proton from resin in the $H^+$ form and they are converted to $NH_4^+$ and $C_6H_5NH_3^+$.

$$R\text{-}CONH_2 + HOH \xrightarrow{RH^+} R\text{-}COOH + NH_3$$



$$R\text{-}CONH\,C_6H_5 + HOH \xrightarrow{RH^+} R\text{-}COOH + C_6H_5NH_2$$

$$C_6H_5NH_2 + RH^+ \longrightarrow R\,C_6H_5NH_3^+$$



Pale yellow resin beads.
(R= alkyl or aryl group)

These ions easily replace $H^+$ from the resin and are detected on the bead surface by means of Nessler's reagent or p-dimethylamino-benzaldehyde.

Such methods can be developed for other organic functional groups as well. In this report we describe a new test for nitriles based on the above considerations.

The second problem in microanalysis is the rapid and selective determination of small quantities of materials. In this case if we wish to obtain accurate results we can not use a technique simpler than spectrophotometry. This is probably the simplest and the most versatile method available for the purpose. of Selectivity and sensitivity ~~and~~ can be achieved by the use of an appropriate color reaction. Since most color reactions are available for cations, more spectrophotometric methods have been developed for cations than for anions. Bromate is one of the anion for which many methods are not avnilable. We have therefore developed a new color reaction for bromate ions which we describe in this thesis.

Of the various methods of separation ion exchange is probably the most important. Ion exchangers may be divided into

two types:

(a) Inorganic ion-exchangers

(b) Organic resins.

During the last few years there has been an increased emphasis on inorganic ion exchangers, particularly of the zirconium phosphate type.

Zirconium phosphate is perhaps the first insoluble salt of a polybasic metal to be used as an ion exchanger. It is the most studied and probably the most useful of all the materials of this type. These materials are prepared by combining oxides of group IV with the more acidic oxides of groups V and VI of the periodic table.

| IV | V | VI |
|---|---|---|
| C | N | O |
| Si | P | S |
| Ge Ti | As V | Se Cr |
| Sn Zr | Sb Nb | Te Mo |
| Pb Hf | Bi Ta | Po W |

These new ion-exchangers have high capacity, give high rates of ion-exchange and are superior to organic resins in their thermal stability and resistance to radiations. They also show high selectivity which can be modified by changing the chemical composition of the material. These substances have therefore attracted considerable attention from nuclear scientists, analytical

chemists, physical chemists, and even pharmaceutical research workers. An indication of the growing interest in this field may be had from the fact that when the book "Ion Exchange" by F. Helfferich[15] was published in 1962 only two pages were devoted to synthetic inorganic ion exchangers and out of this only one page was devoted to the salts of polybasic metals. However, only two years after Helfferich a monograph was published by Amphlett[16] on "Inorganic Ion Exchangers" in 1964. This book is a classic in the field and it led to a revolutionary upsurge of interest in inorganic ion exchangers.

It is, therefore, useful to summarize the progress in the chemistry of inorganic ion exchangers of the generic type of zirconium phosphate from 1964. This has been done under the following heads.

1. Studies on amorphous materials.
2. The crystallization and characterization of ion-exchange materials.
3. The mechanism of ion-exchange.
4. The thermodynamics of ion-exchange.
5. The kinetics of ion exchange.
6. Ion-exchange in fused salts.
7. Ion-exchange between solids.
8. The surface properties of gels.
9. Analytical applications.
10. Miscellaneous.

Amorphous zirconium phosphate like ion-exchange materials, i.e. phosphates[16-19], arsenates[20-23], molybdates[24-27], tungstates[28-3] and antimonates[32,33] of Zr(IV), Sn(IV), Ti(IV) and Th(IV) have been synthesized and their ion exchange behaviour has been studied. Uranyl hydrogen phosphate[34-38], zirconium oxalate[16], titanium selenite[78], zirconium vanadate[66], chromium phosphate[67], Tin(IV) hexacyanoferrate(II)[64], stannous ferrocyanide[65], and hydrated tantalum pentoxide[39] have also been investigated. In four extensive papers Vesely and coworkers have studied the sorption mechanism of cations on uranyl phosphate. The mechanism of the sorption of the di- and tervalent cations on uranyl hydrogen phosphate has been explained in terms of the formation of the simple metal phosphates. Precipitation mechanism for the sorption of tetravalent elements on ammonium uranyl phosphate has been confirmed. For this purpose the solubility products of $UO_2HPO_4 \cdot 4H_2O$, $(UO_2)_3(PO_4)_2 \cdot 4H_2O$, $NH_4UO_2PO_4$ and $(NH_4)_x H_y M^{IV}_{3-x-y}(PO_4)_{3-x-y}$ have been determined. However, the values of solubility products of the alkali uranyl phosphate found by Vesely et al. differ substantially from the values determined by Muraveva et al. and the solubility products series for alkali uranyl phosphates also markedly conflicts with the results of Vesely. Sb/Sn ratio was found to be critical for the stability of amorphous stannic antimonate[32] and the adsorption of the alkali metals on it was similar to ion-120. Hydrated tantalum pentoxide[39] was found to be a good ion-exchange material to work at higher temperatures.

There are three major problems which are faced in analytical applications of inorganic ion exchangers. They are (1) Chemical stability (2) Thermal stability and (3) Specificity.

The greater breakdown of inorganic ion exchanger in simple eluents when compared with organic resins seriously limits their use in practical work. Owing to the presence of interfering ions Kd values are difficult to determine either by spectrophotometry or complexometry. It is therefore very heartening to learn that titanium tungstate[30] shows unusual chemical stability even in 6M-$HNO_3$.

The thermal stability of an ion-exchange material depends upon the cation and the anion present in the exchanger. Titanium vanadate[40], stannic arsenate[21] and stannic selenite[41] are the most thermally stable materials.

The selectivity of an exchanger depends on ion pair formation (discussed above), size of the cavities, the hydrated radii and the charge on the exchanging ion. The ion pair formation in turn depends upon the solubility product of the cation with the anion of the exchanger. The cations with low $K_{sp}$ values have low Kd values and vice versa. Since these materials have not been crystallized it is not yet possible to say anything definite about the size of the cavities.

The crystallization of inorganic ion exchangers is difficult and tedious but it offers many advantages. It was found for

instance that on crystallization thorium arsenate becomes specific for lithium[23] ions while zirconium and tin phosphates[42,43] becomes more stable towards hydrolysis. Therefore, zirconium phosphate[44], zirconium arsenate[45], titanium phosphate[18], titanium arsenate[46], cerium phosphate[47], cerium arsenate[48], thorium arsenate[23], tin phosphate[43] and antimonic acid[49,50] were successfully crystallized. It was found in almost all cases that crystallization adds to the stability and the selectivity of the ion-exchanger. Since crystallization ensures the purity of the product it also facilitates many theoretical studies.

The crystal structure of zirconium phosphate[44] was studied by Clearfield and coworkers who showed that zirconium phosphate has a layered structure. Each layer consists of sheets of zirconium atoms. The phosphate groups are above and below the sheets of metal atoms. They also explained the ion-exchange mechanism on this basis[44,51,52].

In two interesting papers[53,54] Clearfield discusses the mechanism of $Li^+$-$H^+$ and $Na^+$-$H^+$ exchange on $\alpha$-zirconium phosphate. He explains the formation of a hysteresis loop in both cases by the existence of two phase systems containing the unexchanged and the semi-exchanged exchanger. The phases present during the forward and the backward reactions are different and give rise to a hysteresis loop. It is probable that similar studies on crystalline products may give equally valuable results.

Nancollas and coworkers have studied the thermodynamics of cation exchange on zirconium phosphate[55-57]. They have determined the values of $\Delta S$, $\Delta H$, and $\Delta F$ for the exchange reaction,

$$R^-H^+ + M^+ \rightleftharpoons R^-M^+ + H^+$$

and they have interpreted the thermodynamical functions in terms of the nature of the bonding between the alkali metal ion and the matrix of the ion exchanger. It is hoped that such studies will be continued so that a better understanding is obtained of the ion-exchange process. Similar studies have also been reported on anion exchange[58,59].

Nancollas also studied the kinetics of $Na^+$-$H^+$ exchange on crystalline zirconium phosphate. The rate of exchange is initially fast and then becomes slow, suggesting a change in crystal structure[60]. Fuga and Kikonda studied the kinetics of ion exchange between alkali metals and zirconium antimonate[59] in hydrogen form at 25°. They found that the rate of the reaction increases with the atomic number of the cation. It was slower than that for sulphonated resins but more rapid than that for carboxylic resins.

Unfortunately very few studies have been reported on ion exchange in molten salts. One paper by Alberti[61] treats ion exchange on amorphous zirconium phosphate in molten nitrates. He found that lithium ions are greatly preferred over potassium ions by the exchanger.

A recent paper which points to many interesting possibili-

ties is from Clearfield[62]. He found that ion exchange between two solids is possible. Thus if zirconium phosphate in hydrogen form is heated with a salt, e.g., $CoCl_2$ then the following equilibrium exists:

$$CoCl_2 + 2HR \rightleftharpoons R_2Co + 2\,HCl$$

As the volatile acid is removed the reaction proceeds to the right and ion exchange proceeds. Such exchanges should be possible whenever one of the products of ion exchange is volatile at the reaction temperature and can be removed.

Many interesting points emerge from the studies of Murray and coworkers[63] on the surface properties of zirconium phosphate gels. They found that the charge on these gels depends on the exchanger composition and the pH of the solution. Uptakes of electrolytes such as $K^+$ and $Li^+$ are lowest at the zero point of charge and at pH values where the solid is positively charged. These ions are not adsorbed until the gel has a negative surface charge. These phenomena suggest that surface charge is principally responsible for the sorptive and exchange properties of these gels. However, when the exchange leads to the formation of an insoluble phosphate, e.g., $Ag^+ - H^+$ exchange then the surface charge is less important. In this case $Ag^+$ ions are chemisorbed even when the solid is positively charged.

Chromatography on papers impregnated with inorganic ion exchangers of the type zirconium phosphate has been reported

recently and a number of interesting separations have been developed. In some of the studies reported from these laboratories[84] it was observed that these papers are highly selective and they give rapid separations with simple aqueous systems. These papers are useful in rapid evaluation of the analytical potential of an ion-exchange material. The use of mixed solvent systems increases the selectivity of these materials because now solvent extraction and ion exchange mechanisms both play an important role. The spots are more compact than in aqueous systems. The importance of mixed solvent systems for paper chromatography on inorganic papers was first reported by Qureshi and coworkers[85]. It is hoped that these solvents will find increasing use in column chromatography also. Some important separations achieved using these papers are listed in Table II.

The counter ion-matrix interactions are more important in inorganic ion exchangers than in organic resins. They sometimes lead to irreversible adsorption (when the ion is incorporated in the matrix) and often lead to selective or specific separations. Stannic molybdate[25] and stannic tungstate[29] are specific for lead, zirconium vanadate[66] adsorbs K, Na, Ba, Sr, Mg, Cd, Fe, Co, Ni, Pb, Zn, Cu and Ag but does not adsorb Al, Mn, Bi, Ti, and Hg and chromium tripolyphosphate glass is suitable for column operations[87] and can be used for the separations of alkali metals. Distribution coefficients for actinides on zirconium phosphate were determined as a function of $HNO_3$ concentration. Kd values of alkali

TABLE - II

Some important binary, ternary and quarternary separations on papers impregnated with inorganic Ion Exchangers[84].

| Solvent system | Separations achieved | Paper used |
|---|---|---|
| Acetone + Acetic acid + n-Butanol + 4M HCl (1:1:1:1) | $Al^{3+}$ - $In^{3+}$ - $Ga^{3+}$ - $Tl^{3+}$ | Titanium tungstate |
| " " " | $Al^{3+}$ - $Be^{2+}$ - $Ga^{3+}$ - $Tl^{3+}$ | " |
| " " " | $Fe^{2+}$ - $Fe^{3+}$ | " |
| Ethyl Methyl ketone + Acetone + 50% HCl (1:6:1) | $Al^{3+}$ - $Be^{2+}$ - $Fe^{3+}$ | " |
| 1M-Ammonium formate | $Mg^{2+}$ - $Sr^{2+}$ - $Ba^{2+}$ | Stannic tungstate |
| Dioxane + Satd. solution of NaF + 1M-HCl (3:1:6) | $Zr^{4+}$ - $Th^{4+}$ | " |
| Acetyl acetone + Acetone + 50%HCl (7:3:1) | $Zn^{2+}$ - $Mn^{2+}$ - $Ni^{2+}$ | " |
| n-Butanol + 50% $HNO_3$ (6:4) | $Ag^{+}$ - $Cu^{2+}$ - $Au^{3+}$ | " |
| 0.1M-ammonium tartarate in 4M-$NH_4OH$ | $Se^{4+}$ - $Te^{4+}$ | " |
| Me-OH + 10M-HCl + HCOOH (6:2:2) | $Cs^{+}$ - $Rb^{+}$ or $K^{+}$ | Stannic selenite |
| 0.1M-$HClO_4$ | $Al^{3+}$ - $Cr^{3+}$ | " |

TABLE - II(Contd.)

| Solvent system | Separations achieved | Paper used |
|---|---|---|
| 1M-$HClO_4$ | $VO_2^{2+}$ - $V^{4+}$ - $Th^{4+}$ | Stannic selenite |
| Me-OH + 10M HCl + Acetic acid (6:1:4) | $Au^{3+}$ - $Ag^{+}$ - $Pt^{4+}$ | ,, |
| 2M-HCl + 2M-orthophosphoric acid (1:1) | $Sb^{3+}$ - $Sb^{5+}$ | Stannic phosphate |
| n-Butanol + HCl (8:2) | $W^{6+}$ - $Mo^{6+}$ | ,, |

metals on antomonic acid in ammonium nitrate and $HNO_3$ have been determined. On the basis of (the above studies ammonium nitrate was found to be a good eluent) for alkali metals. Numerous difficult separations have been achieved on synthetic inorganic ion-exchangers. Some of the more important are given in Table III.

Reference must also be made to a very thorough study on the hydrolysis of zirconium phosphate by Ahrland and coworkers[79]. They found that at low pH the phosphate release is not primarily due to any hydrolysis but rather to the washing out of the phosphoric acid which adheres very stubbornly to the gel. They also found that high affinity of the exchanger for $Fe^{3+}$ is probably due to the incorporation of iron into the exchanger matrix. The latter explanation may hold good in many other cases also.

TABLE - III

Important Separationsion Inorganic Ion-Exchange Columns

| Cations | Separations from | Exchanger | Eluent | Elution order | Ref. |
|---|---|---|---|---|---|
| $Zn^{2+}$ | $Mn^{2+}$ | Hydrous tin oxide | $H_2SO_4$ | $Mn^{2+}$, $Zn^{2+}$ | 68 |
| $Na^+$, $K^+$ | Each other & other elements. | Ammonium molybdophosphate | $NH_4NO_3$ | $Na^+$, $K^+$ | 69 |
| $Na^+$, $Cs^+$ | $Sr^{2+}$, $Ca^{2+}$ | Hydrous tin oxide | $HNO_3$, $NH_4NO_3$ | $Sr^{2+}$, $Ca^{2+}$ last | 70 |
| $Ca^{2+}$ | $Mg^{2+}$, $Sr^{2+}$ | Titanium tungstate | $HNO_3$, $NH_4NO_3$ | $Ca^{2+}$ last | 71 |
| $Ga^{3+}$ | $Al^{3+}$, $In^{3+}$, $Fe^{3+}$ | ,, ,, | $H_2O$, $HNO_3$ | $Ga^{3+}$ last | 30 |
| $Pb^{2+}$ | Numerous metal ions | ,, ,, | $NH_4NO_3$, $HNO_3$ | $Pb^{2+}$ last | |
| $Hf^{4+}$ | $Zr^{4+}$ | ,, ,, | ,, | $Hf^{4+}$ first | 72 |
| $La^{3+}$ | $Ce^{3+}$, $Pr^{3+}$, $Nd^{3+}$, $Sm^{3+}$ | ,, ,, | ,, | $La^{3+}$ last | |
| $Al^{3+}$ | $In^{3+}$, $Mg^{2+}$ | Stannic arsenate | $H_2O$, $HNO_3$ $NH_4NO_3$ | $Mg^{2+}$ $Al^{3+}$, $In^{3+}$ | 73 |
| $Pb^{2+}$, $UO_2^{2+}$, $Cr^{3+}$ | Numerous metal ions | ,, ,, | ,, | $Pb^{2+}$, $UO_2^{2+}$ $Cr^{3+}$ last | 74 |
| $Mg^{2+}$ | $Ca^{2+}$, $Sr^{2+}$, $Al^{3+}$ | Titanium antimonate | $HCl$, $HNO_3$, $NH_4Cl$ | $Mg^{2+}$ first | 33 |
| $VO^{2+}$ | $Fe^{3+}$, $Al^{3+}$, $Mn^{2+}$, $UO_2^{2+}$, $Zr^{4+}$, $Hf^{4+}$ | ,, ,, | ,, | $VO^{2+}$ first | 75 |

TABLE-III(Contd.)

| Cations | Separations from | Exchanger | Eluents | Elution order | Ref. |
|---|---|---|---|---|---|
| $Fe^{3+}$ | $Al^{3+}$, $Mg^{2+}$, $Ni^{2+}$, $Mn^{2+}$ | Stannic molybdate | $NH_4Cl$, $HNO_3$ | $Fe^{3+}$ last | 76 |
| $Ce^{3+}$ | $Pr^{3+}$, $Nd^{3+}$ | ,, ,, | ,, ,, | $Ce^{3+}$ last | |
| $La^{3+}$ | $Ca^{2+}$, $Sr^{2+}$ $Ba^{2+}$, $Y^{3+}$ | Thorium tungstate | $H_2O$, $NH_4Cl$, HCl | $La^{3+}$ last | 31 |
| $Na^+$ | $K^+$, $Cs^+$ | Stannic phosphate | $NH_4Cl$ | $Na^+$, $K^+$, $Cs^+$ | 17 |
| $Na^+$ | $K^+$ | Zirconium phosphate | | $Na^+$, $K^+$ | 77 |
| $Cs^+$ | $Rb^+$ | ,, ,, | | $Rb^+$, $Cs^+$ | |
| $Cd^{2+}$ | Numerous metal ions | Titanium selenite | $2 \times 10^{-4}$ M $HNO_3$, 0.4% $NH_4Cl$ | $Cd^{2+}$ last | 78 |

Two important points emerge from the lengthy studies of Szirtes[80]. He found that the capacity increases with increase in the precipitation temperature and also with an increase in the proportion of the precipitating anions. Biochinova has published a number of papers on inorganic ion exchangers. One of his exchangers, i.e., zirconiumphthalophosphate[81] may be of some practical value since it retains ion-exchange properties upto 700°.

Finally a few novel applications of inorganic ion-exchange beads may be mentioned. The stannic molybdate beads gave a black

color[82] with iron(II) and are specific for this ion. Stannic arsenate beads in the Fe(III) form have been used as an indicator[83] for the titration of zinc with potassium ferrocyanide.

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# C H A P T E R - II

## ORGANIC AND INORGANIC ION-EXCHANGE BEADS AS INDICATOR IN REDOX AND PRECIPITATION TITRATIONS

Recently ion exchange resins have found some novel analytical applications in the detection and determination of organic functional groups[1-4]. Fujimoto[5] was the first to use resin beads as media for the detection of metal ions using known reactions. However, resin beads are not only more selective and sensitive but they can also lead to the discovery of new colour reactions[6]. A new colour reaction of secondary aromatic amines was discovered in this way and used for the detection of diphenylamine. Resin beads loaded with indicators have also been used for the titration of acids and bases[7,8], for studying the adsorption of silica[9], and for studying the state of exhaustion of resin beads[10]. Honda used such resins to estimate the pH in the resin phase[11,12]. As far as we are aware resin beads have not been used as indicators in precipitation titrations.

The inorganic ion exchangers show great selectivity towards some metal ions. Some times these materials adsorb metal ions irreversibly. In such cases the metal ion is probably incorporated in the matrix and the bead of the exchanger

in this particular form can be used advantageously as an indicator. Thus stannic arsenate[13] adsorbs Fe(III) irreversibly. Stannic arsenate beads in the Fe(III) form can, therefore, be used in the titration of metal ions with ferrocyanide.

## EXPERIMENTAL AND RESULTS

Reagents: Potassium ferrocyanide trihydrate of AnalaR grade was kept in an oven at 100°. for an hour. One gram per liter of sodium carbonate was added to a 0.10M ferrocyanide solution which was prepared by exact weighing. Standard solution of zinc sulphate (0.1M) was prepared and standardized with EDTA. Nitrates of other metal ions were used.

Standard solutions of 0.1N ferrous ammonium sulphate, 0.1N potassium dichromate, 0.1N silver nitrate were prepared by direct weighing from B.D.H. 'AnalaR' grade reagents. The ceric sulphate solution was standardized against arsenious oxide.

Dowex 50 W X 8 (20 - 50 mesh) resin beads were used. The beads in the $Na^+$ form were sorbed in an alcoholic solution of diphenylamine and in the $H^+$ form sorbed in p-dimethylamino-benzylidene rhodanine for use in redox titrations and titrations with silver ions respectively.

Procedure:

(a) *Determination of Zn(II), Pb(II), Ag(I) and Cd(II).* To metal ion solutions were added five ml of the appropriate acid solution (1N acetic acid for lead, silver and cadmium and 1N hydrochloric

acid for zinc), one ml of distilled alcohol and three to four beads in Fe(III) form. This was titrated with a standard solution of potassium ferrocyanide by adding it dropwise from a 5 ml microburette. The solution was vigorously shaken after the addition of each drop at the end point. A sharp colour change from yellow to blue due to the formation of prussian blue is obtained on the resin beads. The results are given in Table IV.

TABLE - IV.

Determination of Zn(II), Pb(II), Ag(I) and Cd(II)

| Concentration of ferrocyanide(Molar) | Cations taken (mg) | Cations found (mg) | % Error |
|---|---|---|---|
| 0.01 | 0.6732 Zn(II) | 0.6732 Zn(II) | 0.00 |
| 0.01 | 0.3315 Zn(II) | 0.3315 Zn(II) | 0.00 |
| 0.01 | 0.5304 Zn(II) | 0.5304 Zn(II) | 0.00 |
| 0.01 | 103.50 Pb(II) | 104.00 Pb(II) | + 0.4 |
| 0.01 | 2.07 Pb(II) | 2.07 Pb(II) | 0.00 |
| 0.01 | 10.80 Ag(I) | 10.85 Ag(I) | + 0.4 |
| 0.01 | 15.40 Ag(I) | 15.43 Ag(I) | + 0.3 |
| 0.01 | 5.25 Cd(II) | 5.26 Cd(II) | + 0.4 |
| 0.01 | 0.225 Cd(II) | 0.226 Cd(II) | + 0.2 |

(b) Determination of Fe(II) and $Na_2S_2O_3$:

To a 5 ml of Fe(II) solution were added 5 ml of 5N sulphuric acid, and one ml of 85% phosphoric acid, followed by three to four resin beads sorbed in diphenylamine. The solution was titrated with a standard solution of potassium dichromate, ceric sulphate, or potassium permanganate by adding it dropwise from a 5 ml microburette. The solution was vigorously shaken after the addition of each drop. At the equivalence point a sharp colour change from yellow to blue appeared at the resin surface. For the determination of $Na_2S_2O_3$, its solution (5 ml) was kept in a beaker followed by 5 ml of 5 N sulphuric acid. The titration was carried out against ceric sulphate solution. The results are summarized in Table V.

TABLE - V.

Determination of Fe(II) and $Na_2S_2O_3$

| Concentration of titrant | Amount taken (mg) | Amount found (mg) | % Error |
|---|---|---|---|
| 0.1N $K_2Cr_2O_7$ | 4.48 Fe(II) | 4.49 Fe(II) | + 0.22 |
| 0.1N $K_2Cr_2O_7$ | 5.60 Fe(II) | 5.61 Fe(II) | + 0.17 |
| 0.1N $K_2Cr_2O_7$ | 8.50 Fe(II) | 8.52 Fe(II) | + 0.23 |
| 0.01N $Ce(SO_4)_2$ | 5.60 Fe(II) | 5.61 Fe(II) | + 0.17 |
| 0.01N $Ce(SO_4)_2$ | 7.84 Fe(II) | 7.86 Fe(II) | + 0.25 |
| 0.01N $KMnO_4$ | 5.60 Fe(II) | 5.61 Fe(II) | + 0.2 |
| 0.005N $KMnO_4$ | 0.560 Fe(II) | 0.561 Fe(II) | + 0.2 |
| 0.01N $Ce(SO_4)_2$ | 5.930 $S_2O_3^{--}$ | 5.960 $S_2O_3^{--}$ | + 0.5 |
| 0.01N $Ce(SO_4)_2$ | 1.150 $S_2O_3^{--}$ | 1.155 $S_2O_3^{--}$ | + 0.4 |

(c) Determination of Chloride, bromide and iodide:

To a 5 ml solution of the metal halide were added a few beads sorbed in p-dimethylaminobenzylidene rhodanine. In the case of chloride and bromide 5 ml of alcohol was also added. On titration with silver nitrate a sharp colour change from yellow to violet was observed at the end point. The results are given in Table VI.

TABLE - VI.

Determination of chloride, bromide and iodide

| Concentration of silver nitrate | Halide taken (mg) | Halide found (mg) | % Error |
|---|---|---|---|
| 0.05N | 1.725 $Cl^-$ | 1.730 $Cl^-$ | + 0.28 |
| 0.05N | 3.550 $Cl^-$ | 3.561 $Cl^-$ | + 0.30 |
| 0.05N | 7.100 $Cl^-$ | 7.120 $Cl^-$ | + 0.28 |
| 0.05N | 4.00 $Br^-$ | 4.02 $Br^-$ | + 0.30 |
| 0.05N | 20.00 $Br^-$ | 20.01 $Br^-$ | + 0.30 |
| 0.05N | 12.70 $I^-$ | 12.70 $I^-$ | + 0.10 |
| 0.05N | 25.40 $I^-$ | 25.41 $I^-$ | + 0.30 |

(d) Simultaneous determination of Zn(II) and $Cl^-$ in a mixture of zinc chloride and sodium chloride solution.

To a mixture of zinc chloride and sodium chloride 5 ml of alcohol and a few beads sorbed in p-dimethylaminobenzylidene rhodanine were added. The chloride solution was titrated with a

standard solution of silver nitrate till a sharp colour change from yellow to violet on the resin phase was observed. Five ml of 1N hydrochloric acid were added to precipitate the excess of silver ions and to make the solution acidic. Fe(III) beads were then added and zinc determined by titration with ferrocyanide. The results are given in Table VII.

TABLE - VII.

Simultaneous determination of Zn(II) and $Cl^-$

| $Cl^-$ given (mg) | $Cl^-$ found (mg) | % Error | Zn(II) given (mg) | (Zn(II) found (mg) | Error |
|---|---|---|---|---|---|
| 0.439 | 0.440 | + 0.23 | 0.0996 | 0.1000 | + 0.4 |
| 0.393 | 0.380 | - 3 | 0.0843 | 0.0840 | - 0.3 |
| 0.415 | 0.416 | + 0.2 | 0.09200 | 0.0925 | + 0.5 |
| 0.370 | 0.366 | - 1 | 0.0760 | 0.0750 | - 1.2 |

(d) Simultaneous determination of silver and lead in a mixture of silver nitrate and lead nitrate.

The silver nitrate-lead nitrate mixture was taken in a burette and the titrant was added drop by drop to the sodium chloride solution to which 5 ml of alcohol had already been added. p-dimethylaminobenzylidene rhodanine beads were also used as indicators. At the equivalence point silver was precipitated as silver chloride and lead nitrate remained in the beaker. A few drops of sodium chloride were added at the equi-

valence point to precipitate excess silver (this minimizes the error in the determination of lead). 5 ml of 1N acetic acid were added and lead was titrated with potassium ferrocyanide using Fe(III) beads as indicator. The results are summarized in Table VIII.

TABLE - VIII.

Simultaneous determination of lead and silver

| Silver given (mg) | Silver found (mg) | %Error | Lead given (mg) | Lead found (mg) | %Error |
|---|---|---|---|---|---|
| 1.600 | 1.605 | + 0.3 | 1.200 | 1.200 | 0.00 |
| 1.400 | 1.401 | + 0.07 | 1.40 | 1.39 | - 0.07 |
| 1.200 | 1.200 | 0.00 | 1.60 | 1.59 | - 0.06 |
| 0.900 | 0.900 | 0.00 | 1.10 | 1.10 | 0.00 |

(f) Determination of chloride in a coloured solution:

The chloride in a mixture of $Co^{++}$ and $Cl^{-}$ ions is determined as given in (c). The addition of a few ml saturated cobalt nitrate solution intensifies the color but does not effect the end point.

One should take care that the drop of titrant should not fall on the resin beads. A blank correction should be made in each case. The results are summarized in Table IX.

TABLE - IX.

Comparison of the beads method with Volhard's method in the titration of $Cl^-$ in $CoCl_2$.

| Volhard's method | | | Beads method | | |
|---|---|---|---|---|---|
| Chloride taken (mg) | Chloride found (mg) | % Error | Chloride taken (mg) | Chloride found (mg) | % Error |
| 6.35 | 3.19 | 49 | 6.35 | 6.30 | 0.7 |
| 13.78 | 9.88 | 25 | 13.78 | 12.80 | 0.1 |
| 9.88 | 6.55 | 30 | 9.88 | 9.80 | 0.2 |

(g) To find the lower limit of chloride concentration for satisfactory estimation, chloride solutions of different concentrations were titrated by this method. The results are summarized in Table X.

TABLE - X.

Titration of 0.001N chloride ions against dilute solutions of silver nitrate.

| Concentration of silver nitrate | Concentration of sodium chloride | Chloride taken (mg) | Chloride found (mg) | % Error |
|---|---|---|---|---|
| 0.005N | 0.001N | 0.0100 | 0.1078 | 0.9 |
| 0.002N | 0.001N | 0.1060 | 0.1065 | 0.4 |
| 0.001N | 0.001N | 0.1060 | 0.1064 | 0.3 |

(h) Effect of diverse ions in Zn(II) determination:

To a solution containing 0.6732 mg/5 ml of Zn(II), the following ions are added in milligrams given in parentheses. No interference is noticed in the zinc determination.

Ba(II)(100), Sr(II)(100), Na(I)(340), Al(III)(40), Ca(II)(120), $NH_4$(I)(40).

$S_2O_3^{--}$, $ClO_3^-$ and $ClO_4^-$ do not interfere. The chloride solutions of the above metal ions and the potassium salts of sulphite, thiosulphate, thiocyanate, chlorate and perchlorate were used in the determination.

(i) Effect of diverse ions on titrations of Zn using stannic arsenate beads in Fe(III) forms.

The following ions did not interfere in the titration of 0.6732 mg/5 ml of Zn(II). The mgs of ions tolerated are given in parentheses:

Ba(II)(120), Al(III)(60), $NH_4$(I)(60), Na(I)(320), Ca(II)(140).

## DISCUSSION

The resin bead indicators present some useful and interesting features and are therefore more versatile than the conventional indicators. The resin bead method is applicable for the accurate determination of $Cl^-$, $Br^-$ and $I^-$. It is therefore superior to the Mohr's method which cannot be used for the determination of iodides and thiocyanates. Further the Mohr's titration based on the formation of orange red silver chromate at the end point, is possible only in the pH range of 7-10.5. Silver chromate is soluble in acids and it cannot be precipitated in their presence. The bead method can be used with accuracy from pH 2-7. At pH less than 2 the method is inaccurate. Volhard's method is undoubtedly superior to Mohr's method, but it cannot be used if the solution itself has an intense colour. Thus in the titration of cobalt chloride the Volhard's method gives wrong results while the beads method is accurate. It is also superior to the adsorption indicator method as it is possible to titrate 0.001N chloride solution by this method. It is not possible to titrate chloride solution more dilute than 0.005N using fluorescein as an indicator.

Another novel feature is that resin bead can be used for the simultaneous determination of two substances at the same time. Thus Zn(II) and $Cl^-$ can also be determined quantitatively without

## DISCUSSION

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Another novel feature is that resin bead can be used for the simultaneous determination of two substances at the same time. Thus Zn(II) and $Cl^-$ can also be determined quantitatively without

any prior separation. Silver and lead can also be determined simultaneously, because it is possible to add different resin bead indicators in stages. This is not the case with conventional indicators.

Another advantage of the bead method is the fact that selective, specific and sensitive spot test reagents can be appropriately used for volumetric titrations. The use of *p-dimethylaminobenzylidene rhodenine is a case in point.* It has been used as an internal indicator for the titration of $AgNO_3$ with KCl or KBr. It was found that the titration is possible upto a concentration of 6N for nitric acid and 10N for sulphuric acid[14].

The great advantage of the resin bead indicator is that it replaces different indicators used in the classical methods by a single indicator when different species are titrated against the same titrant. Thus the titration of the different metal ions e.g., Zn(II), Pb(II), Ag(I) and Cd(II) have been carried out using resin bead in Fe(III) form as the indicator. Emphasis has been given to the determination of Zn(II) because its estimation is of great practical importance.

The method is particularly useful in dilute solutions, where the precipitates are not so dense and the color change on the beads can be easily detected at the equivalence point. In more concentrated solutions, the beads are not visible due to thick precipitation, but the colour change on the resin phase

can be seen by raising the beaker above the eye level and viewing the beads at the bottom.

As zinc ferrocyanide is more soluble than the prussian blue, when the zinc titration is performed with ferrocyanide in aqueous medium, the end point is obtained rather early and the results are erroneous. However, if alcohol is added before the titration is started, accurate results are obtained. This is possible because the addition of alcohol lowers the solubility product of zinc ferrocyanide. It will also lower the solubility product of iron ferrocyanide but it is possible that the solubility product of zinc ferrocyanide is comparatively more affected than the solubility product of prussian blue. Similarly, addition of alcohol may improve the ferrocyanide end point with Pb(II), Ag(I), and Cd(II). The addition of alcohol has a remarkable effect on the interference by diverse ions. Thus without alcohol Ba(II) interfered in the zinc titration even in the 1:1 ratio. However, in the presence of alcohol even more than 100 times of Ba(II) did not interfere. The same is true for other ions also. This is because the addition of alcohol suppresses the ionisation of these electrolytes and prevents their interference. Stannic arsenate beads give even better results. Since Fe(III) is irreversably adsorbed, the addition of large quantities of interfering ions does not affect the titrations.

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# C H A P T E R - III

## AN ION EXCHANGE METHOD FOR THE DETECTION OF NITRILES

Very few tests are available for the detection of nitriles[1]. Detection is usually based either on some general test for several functional groups, or on the interferences caused by the nitriles in a particular test. None of the tests is specific for nitriles. Hydroxamic acid has been suggested for the detection of nitriles[2]. The test is suitable for certain derivatives of carboxylic acids, such as esters, anhydrides and acid chlorides, and for trichloromethyl groups. Amides and anilides provide the main interference. Nitriles have also been detected and differentiated from amides by performing two tests. The soda lime - methanolic copper sulphate test[3] gives a blue colour with nitriles, if no amide is present, whereas the mercury(II) chloride - bromothymol blue test[3] is negative for nitrile if no N, N'-disubstituted amide is present and positive for monosubstituted or unsubstituted amides. The test is an improvement over the hydroxamic acid test, but amines and compounds containing olefinic and acetylenic bonds or $\alpha$-hydrogen atoms interfere in both cases.

Recently, ion exchange resin have been used for the

detection of esters, amides, imides and anilides[4,5] and for the determination of aliphatic unsubstituted amides and esters[6]. The resin beads act simultaneously as catalyst and as a detection medium. In this test the same technique has been successfully applied and the work has been extended for the detection of nitriles. Moreover the test is highly selective for nitriles and can be used to differentiate nitriles from unsubstituted amides.

## EXPERIMENTAL AND RESULTS

Reagents: All the reagents used were of reagent grade. Solution of nitriles were prepared in distilled alcohol. Conductivity water was prepared by first deionizing water then distilling it from alkaline permanganate.

Dowex 50 W X 8 (20-50 mesh) was used in the $H^+$ form. The resin was regenerated and washed with conductivity water until no pink color was obtained with Nessler's reagent.

Detection of Nitriles: The following two tests are necessary for the detection of nitriles.

Test I. To one drop of each of the test solution and water add two drops of concentrated sulphuric acid in semimicro-test tube. Heat the contents slowly for a few minutes on a low flame. Cool, add a few resin beads and one drop of water and heat (not boil) again. Decant, leaving behind the resin beads. Wash the beads by decantation with 4-5 portions of conductivity water. Transfer the beads to a spot plate and dry them with filter paper. Add a drop of Nessler's reagent. A pink or red color on the resin beads indicates a positive test.

Test II. Mix a few mg of test substance with two drops

of water in a semimicro test tube. Add a few resin beads and heat (not boil) on a low flame. Cool the beads and wash as described above. Transfer to a white spot plate and test with one drop of Nessler's reagent. A pink color indicates a positive test.

Nitriles give a positive response with Test-I and a negative response with Test-II. For unsubstituted amides and imides both tests are positive. It is therefore possible to distinguish between unsubstituted amides and nitriles. Other organic compounds give a negative response with the recommended tests.

The nitriles shown in Table XI were detected by the recommended method. Mandelonitrile gave the test for amides. Benzyl nitrile gave the negative test.

The following unsubstituted amides and imides were detected and thus differentiated from nitriles.

Oxamide, chloroacetamide, N-Valeramide, foramide, succinamide, salicylamide, acetamide, propionamide, succinimide and phthalimide.

TABLE - XI.

Limit of identification of nitriles

| Nitriles | Amount detected (mg) | Limiting dilution |
|---|---|---|
| Acetonitrile | 1.05 | 1:500 |
| Propionitrile | 0.137 | 1:500 |
| Butyronitrile | 0.305 | 1:150 |
| Acrylonitrile | 0.215 | 1:200 |
| Benzonitrile | 1.03 | 1:500 |
| Chloroacetonitrile | 0.377 | 1:150 |
| Cyanoacetic acid | 0.425 | 1:100 |

Negative tests were given by the following organic compounds:

Alcohols: Methanol, ethanol, n-propanol, iso-propanol, n-butanol, iso-butanol, glycerol, ethylene glycol.

Acids: Oxalic, formic, acetic, propionic, benzoic, tartaric and sulphanilic acids.

Hydrocarbons and their derivatives: Benzene, bromobenzene, nitrobenzene, chlorobenzene, chloroform, carbon-tetrachloride, toluene and cyclohexane.

Aldehydes: Acetaldehyde, crotonaldehyde and chloral hydrate.

Ketones: Acetone, cyclohexanone, methyl ethyl ketone, di-isobutyl ketone, methylisobutyl ketone, and acetyl acetone.

Carbohydrates: Fructose, raffinose and sucrose.

Ethers: Ether, anisole and dioxane.

Esters: Ethyl acetate, ethyl acetoacetate, methyl benzoate, diethyl malonate, tributyl-phosphate.

Anilides: Acetanilide and oxanilide.

Phenols: Phenol and o-cresol.

Amines: Methyl amine, dimethyl amine, trimethyl amine, diethanol amine, triethanol amine, aniline and diethylaniline.

Heterocyclic bases: Pyridine.

Detection of Nitriles in the presence of foreign substances:

Nitriles can be detected in the presence of foreign substances. Some results for propionitrile are given in Table XII.

TABLE - XII.

Detection of propionitrile in presence of foreign substances.

| Foreign substances | Amount added (mg) | Nitrile detected (mg) | Limiting dilution |
|---|---|---|---|
| Formic acid | 61 | 2.76 | 1:200 |
| Benzene | 4395 | 0.55 | 1:200 |
| Chlorobenzene | 73.70 | 0.55 | 1:200 |
| Methylamine | 6.00 | 2.76 | 1:20 |
| Cyclohexane | 72.52 | 16.52 | 1:20 |
| Sucrose | 5.00 | 2.76 | 1:200 |
| Phenol | 53.75 | 2.76 | 1:200 |
| n-Butanol | 40.50 | 0.55 | 1:200 |
| Ethyl acetate | 45.05 | 1.37 | 1:50 |
| Ether | 35.40 | 1.37 | 1:50 |
| Pyridine | 19.66 | 5.50 | 1:20 |
| Acetanilide | 0.50 | 2.76 | 1:20 |

## DISCUSSION

Cation exchange resins in the hydrogen form are very effective in the hydrolysis of unsubstituted amides and imides[5]. The corresponding acid and ammonium ion are formed, and the resin beads in the ammonium form give a red or pink color with Nessler's reagent as described in Test II. Nitriles are not hydrolyzed, hence this test is negative. Nitriles can be hydrolyzed either with sodium hydroxide or with dil. $H_2SO_4$. The later was chosen because it retains ammonia, and conversion of $H^+$ form resin in $NH_4^+$ form takes place. If sodium hydroxide is taken, ammonia gas passes out from the solution and thus a negative test is obtained with Nessler's reagent.

$$X\,CN + HOH \xrightarrow[\text{heat}]{\text{dil. } H_2SO_4} X\,CO\,NH_2 \xrightarrow{RH^+} X\,COOH + NH_3$$

$$X\,COOH + NH_3 \longrightarrow X\,COONH_4$$

$$RH^+ + X\,COO\,NH_4 \longrightarrow \xrightarrow{R\,NH_4^+} + X\,COOH$$

Positive test with Nessler's reagent.

$$XCN + HOH \xrightarrow[\text{heat}]{RH^+}$$ hydrolysis does not take place

Negative test with Nessler's reagent.

(X = alkyl or aryl group)

A positive test is obtained when a drop of Nessler's reagent is added to the resin beads. Unsubstituted amides or imides are also hydrolyzed with dil. $H_2SO_4$ and test I is positive for them. Benzyl nitrile gives a negative test, probably because it does not hydrolyze. The indications given by the two tests are summarized in Table XIII. All the available nitriles were run with a number of organic compounds and the results were satisfactory.

TABLE - XIII

Tests for nitriles, unsubstituted amides, imides and other organic compounds.

| Compounds | Test I | Test II |
|---|---|---|
| Nitriles | Positive | Negative |
| Unsubstituted amides and imides. | Positive | Positive |
| Other organic compounds | Negative | Negative |

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# C H A P T E R - IV

## A CRITICAL STUDY OF SOME TITANIUM BASED EXCHANGERS IN A FEW AQUEOUS AND MIXED SOLVENT SYSTEMS

Since the classical work by Amphlett[1], numerous synthetic inorganic ion exchangers have been synthesized and their properties have been studied. However, it is not possible to compare the relative merits and draw-backs of these exchangers owing to a number of factors. First of all, the methods of preparation of the same ion exchanger by different workers are not the same. It has been shown that the selectivity of an exchanger depends not only upon its composition but also upon the pH at which the precipitation is performed. Secondly, in the study of properties it is necessary that the same procedure should be followed so that the results can be correctly evaluated. Thirdly, sometimes the data which are available for other exchangers are missing in a particular case and hence comparison becomes difficult. For these reasons it is important that the various ion-exchangers should be synthesized again and all their properties be studied by the same workers. Szirtes[2] made an interesting study of the phosphates of titanium, zirconium and chromium and compared to their ion-exchange properties. Such studies are unfortunately not many. We have therefore decided to investigate the various

insoluble compounds of titanium[3-7], i.e., titanium molybdate, titanium antimonate, titanium selenite, titanium arsenate, and titanium tungstate. We have chosen for comparison those samples of the particular exchangor which are reported to be most stable. This comparison has given some general conclusions regarding the properties of the inorganic ion exchangers, which may prove very useful in the proper selection of the material.

Another limitations of the earlier studies on inorganic ion exchangers is in the selection of eluents. Almost all the eluent selected are aqueous solutions of simple salts. We have extended the investigation of the analytical properties of the exchangor in mixed solvent systems or in less common aqueous systems. The results obtained are described in this Chapter.

## EXPERIMENTAL AND RESULTS

Reagents: 15% w/v titanic chloride (B.D.H.), antimony pentachloride (B.D.H.) of density 2.3 g/ml, sodium tungstate (B.D.H. AnalaR), sodium arsenate and sodium selenite (Riedel) were used. All other reagents used were of AnalaR grade.

Apparatus: pH measurements were made with 'Elico' pH meter model LI-10, Bausch and Lomb spectronic 20 colorimeter was used for spectrophotometric determinations. The equilibrium in the distribution coefficient determination was attained by shaking the mixture in a 'SICO' temperature controlled shaker.

Preparation of the Samples: Five samples were prepared separately by mixing the solution of titanium(IV) chloride with sodium tungstate, sodium arsenate, sodium selenite, sodium molybdate and antimony pentachloride. The conditions of preparation are given in Table XIV. In the case of titanium antimonate the pH was adjusted with the help of liquor ammonia. The precipitates thus obtained were allowed to stand for 24 hours at room temperature and then washed with distilled water by decantation, filtered and dried at 40°. Only titanium tungstate was dried at 80°. The dry product broke down into small particles

when immersed in water. It was converted into the hydrogen form by treatment with 2M nitric acid and finally washed with demineralized water. All the samples were again dried at 40°. except titanium tungstate which was dried at 80°.

TABLE - XIV

Conditions for the synthesis of some titanium based exchangers

| Exchangers | Concentration of Ti(IV) | Concentration of anionic species | Mixing ratio Ti:A | pH |
|---|---|---|---|---|
| Titanium tungstate | 0.30M | 0.30M sodium tungstate | 1:1 | $\simeq$ 1 |
| Titanium antimonate | 0.10M | 0.10M antimony pentachloride | 1:1 | $\simeq$ 2 |
| Titanium arsenate | 0.05M | 0.05M sodium arsenate | 1:1 | $\simeq$ 2 |
| Titanium selenite | 0.05M | 0.05M sodium selenite | 1:2 | $\simeq$ 2 |
| Titanium molybdate | 0.025M | 0.025M sodium molybdate | 2:1 | $\simeq$ 2 |

A = anionic species

Composition of the Samples:

1. Titanium antimonate: 200 mg of the exchanger was dissolved in concentrated hydrochloric acid, and antimony was precipitated as antimony sulphide. Antimony in the precipitate was determined

volumetrically with sodium thiosulphate[8] and titanium in the filtrate was determined with ferric ammonium sulphate[9].

II. Titanium tungstate: The exchanger (200 mg) was dissolved in 20 ml. concentrated hydrochloric acid. A known quantity of sodium molybdate was added to precipitate tungsten completely with ∝-benzoin oxime[10]. Titanium was estimated in the filtrate as usual[9].

III. Titanium arsenate: 200 mg of the exchanger was dissolved in concentrated hydrochloric acid and arsenate was precipitated as arsenic sulphide. Arsenic in the precipitate was determined using Volhard's[11] method while titanium was titrated as earlier[9].

IV. Titanium selenite: 200 mg of the exchanger was dissolved in 20 ml of concentrated hydrochloric acid. The solution was diluted to 100 ml with water and selenium was determined gravimetrically by precipitating it with sulphur dioxide[12]. The titanium was determined volumetrically[9]. The results are given Table XV.

Chemical stability:

0.5 g of the exchanger was shaken in the flask with 50 ml of the solution concerned in a temperature controlled shaker for six hours till equilibrium was reached. The undissolved portion of the exchanger was removed by filtration. Titanium, antimony,

tungsten, arsenic, selenium and molybdenum were determined in the filtrate, spectrophotometrically by hydrogen peroxide[13], Rhodamine B[14], Ammonium thiocyanate[15], molybdenum blue[16], diamino-benzidene[17] and ammonium thiocyanate[18] methods respectively (Fig. 1).

Ion Exchange Properties:

The ion exchange capacity, determined by the standard method[9] is given in Table XV. It was also determined at different pH values by the use of the batch process. The results are plotted in Figure 2. All the samples were heated at different specified temperatures for two hours and the ion exchange capacity was determined in each case by the earlier method[19]. The results are shown in Figure 3.

TABLE - XV.

The ion exchange capacities and the compositions of some titanium based exchangers.

| Exchanger | Ion exchange capacity $m.equiv.g^{-1}$ | Reported capacity | Composition | Reported composition |
|---|---|---|---|---|
| Titanium tungstate | 0.58 | 0.82 | 1:1.1 | 1:1.1 |
| Titanium arsenate | 0.99 | 0.93 | 1:1.8 | 1:2 |
| Titanium antimonate | 0.77 | 0.71 | 1:1.4 | 1:1.4 |
| Titanium selenite | 0.58 | 0.78 | 1:1.2 | 1:1.35 |
| Titanium molybdate | 1.08 | 1.05 | - | - |

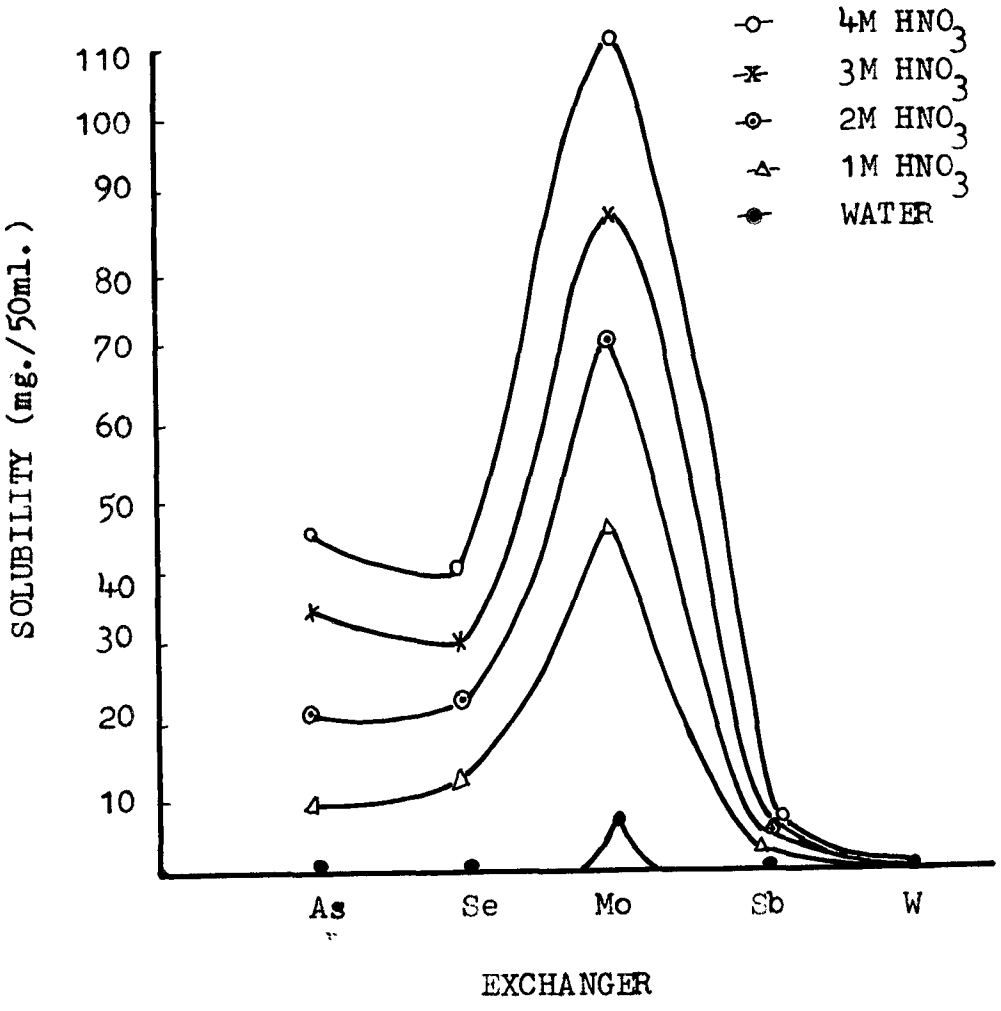



Fig.1 Solubility Of Ti(IV) Based Exchangers

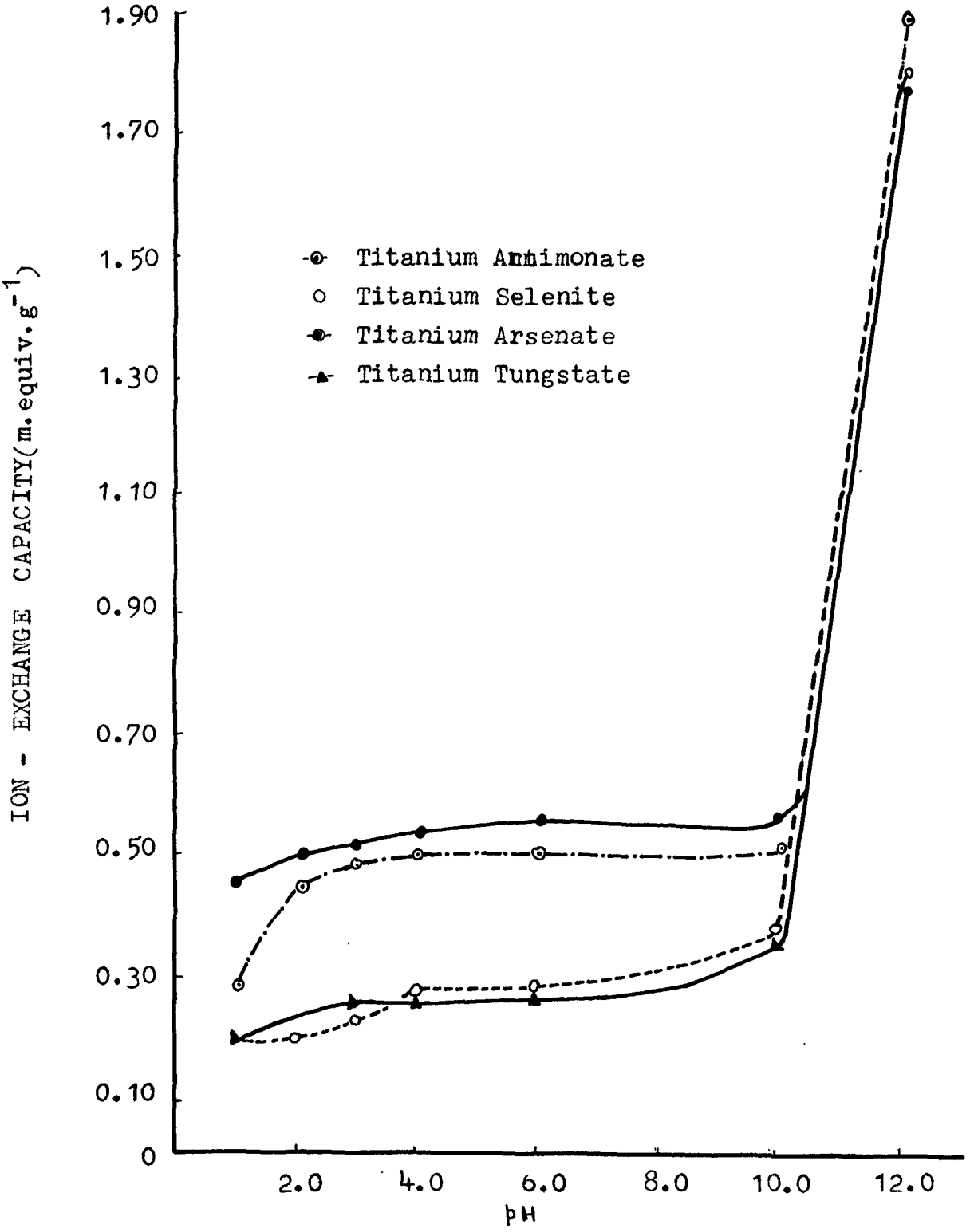



Fig. 2 Ion - Exchange Capacity As A Function Of pH

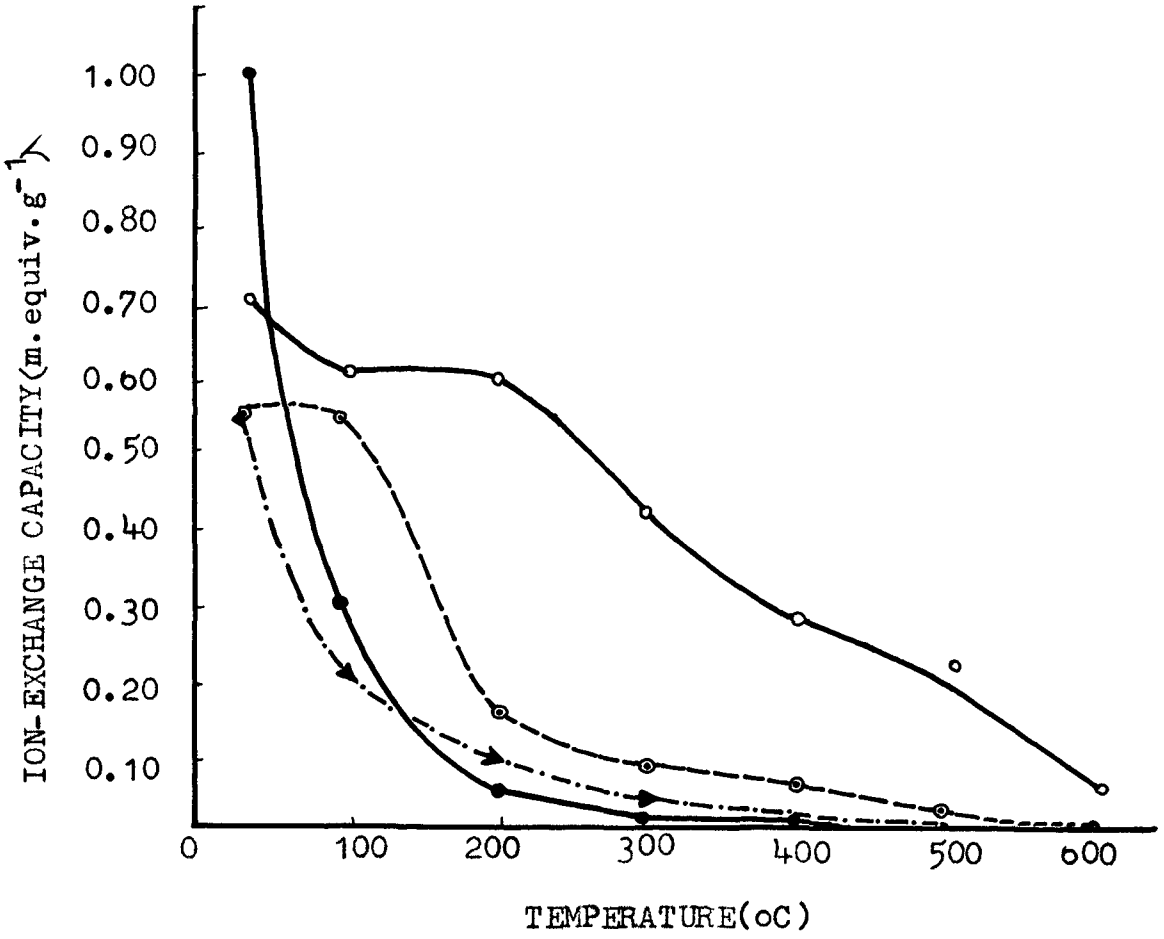



Fig.3 Ion-Exchange Capacity As A Function Of Temperature

-●- Titanium Arsenate

-○- Titanium Antimonate

-◎- Titanium Tungstate

-▲- Titanium Selenite

Distribution Studies:

Distribution coefficients of 26 metal ions in water, nitric acid of different concentrations, 0.1M ammonium nitrate, 0.1M formic acid, and some acetone-nitric acid mixtures were determined. For this purpose 0.5 g of the exchanger concerned was shaken with 50 ml of the solution for 6 hrs. The amount of the cations in the solution was estimated by the EDTA titration and the Kd values were calculated by the expression:

$$Kd = \frac{I - F}{F} \times \frac{50}{0.5}$$

Where I is the volume of EDTA consumed by the original solution and F is the volume of EDTA consumed after equilibrium.

The loading of the cation was 3% of the ion exchange capacity of the ion exchanger. The results are given in figures 4 - 13.

Separations:

Separations of Cd(II) from Hg(II), Ba(II)-La(III), Zn(II) - Pb(II) and Cu(II) - Pb(II) have been achieved on the basis of Kd values. The elution curves for the separations achieved are given in figures 14-15.

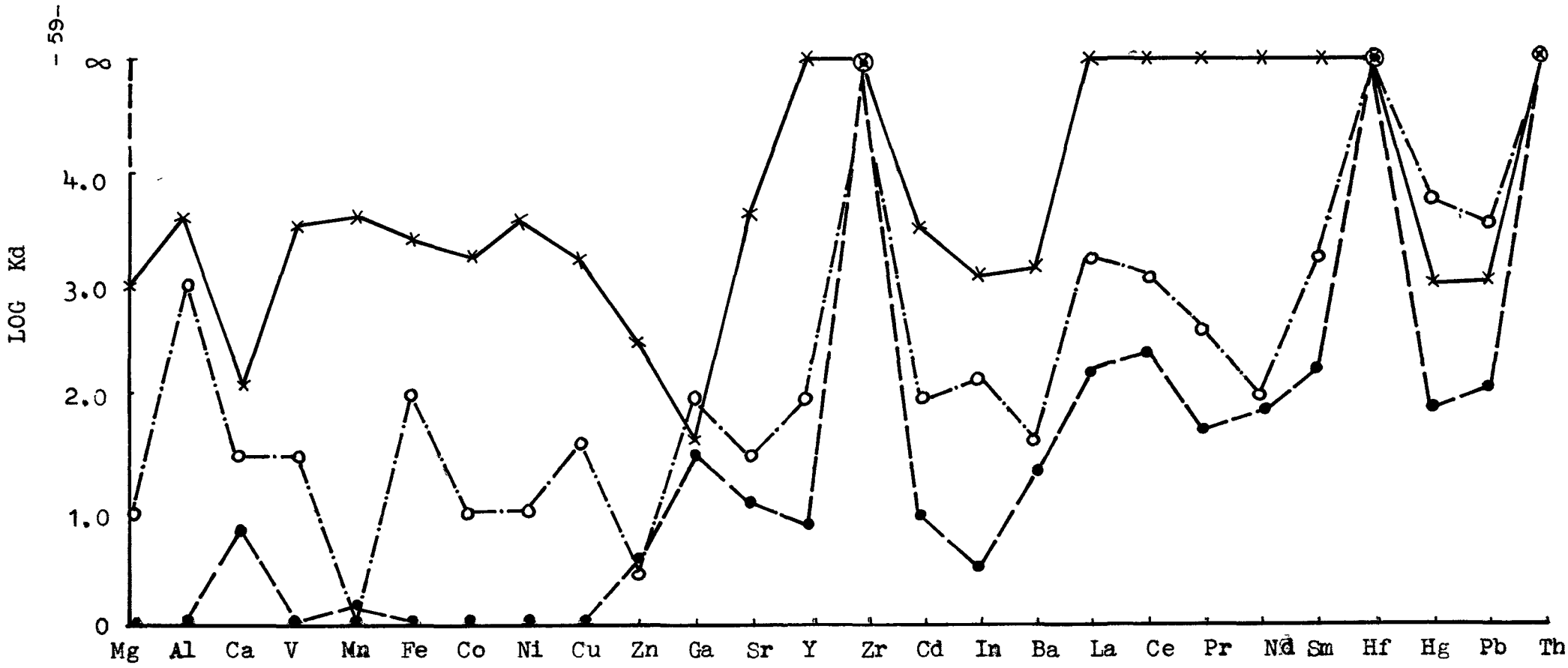



Fig.4 Distribution Coefficients of Metal Ions On Titanium Antimonate.

-x- Water

-o- 0.01M $HNO_3$

-●- 0.10M $HNO_3$

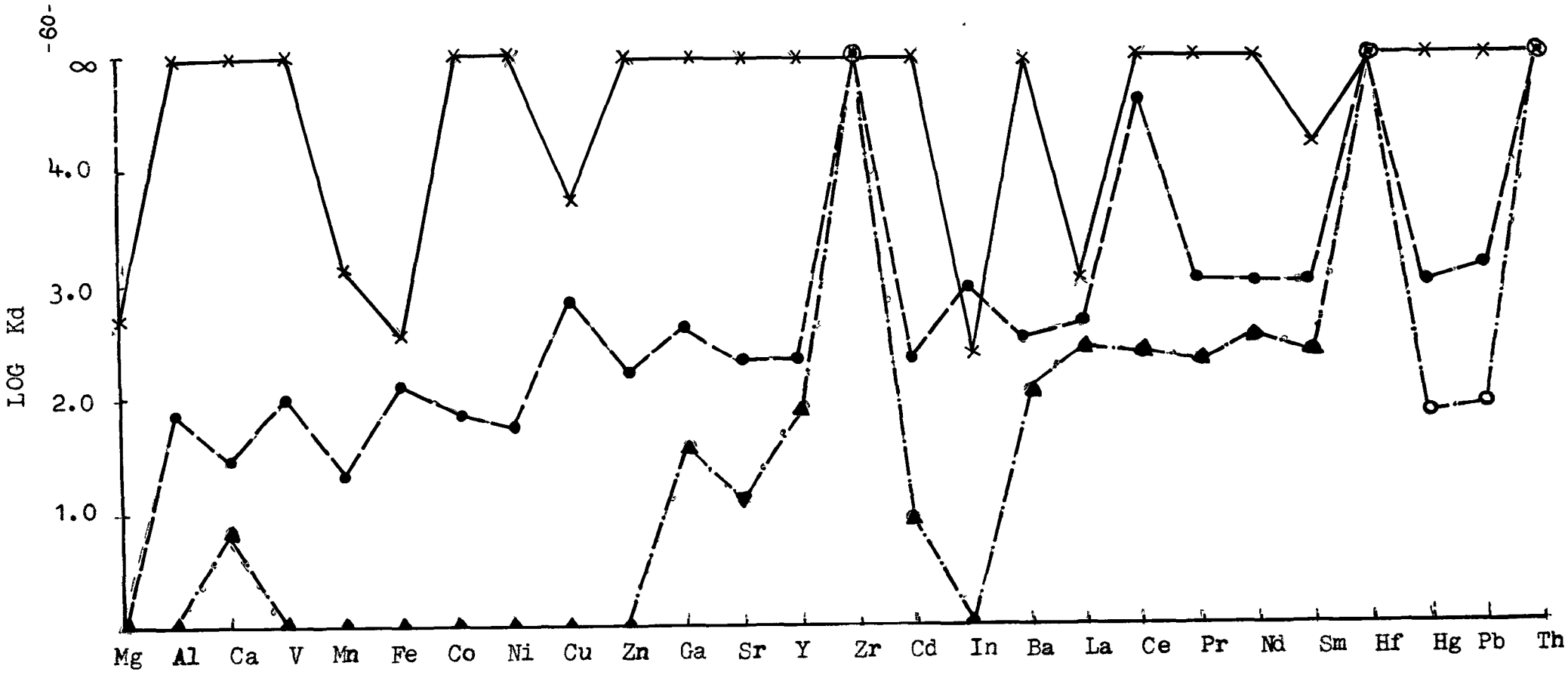



Fig.5 Distribution Coefficients of Metal Ions on Titanium Antimonate.

-x- 0.1M HCOOH

-o- 0.1M $NH_4$ $NO_3$

-▲- 0.1M $HNO_3$

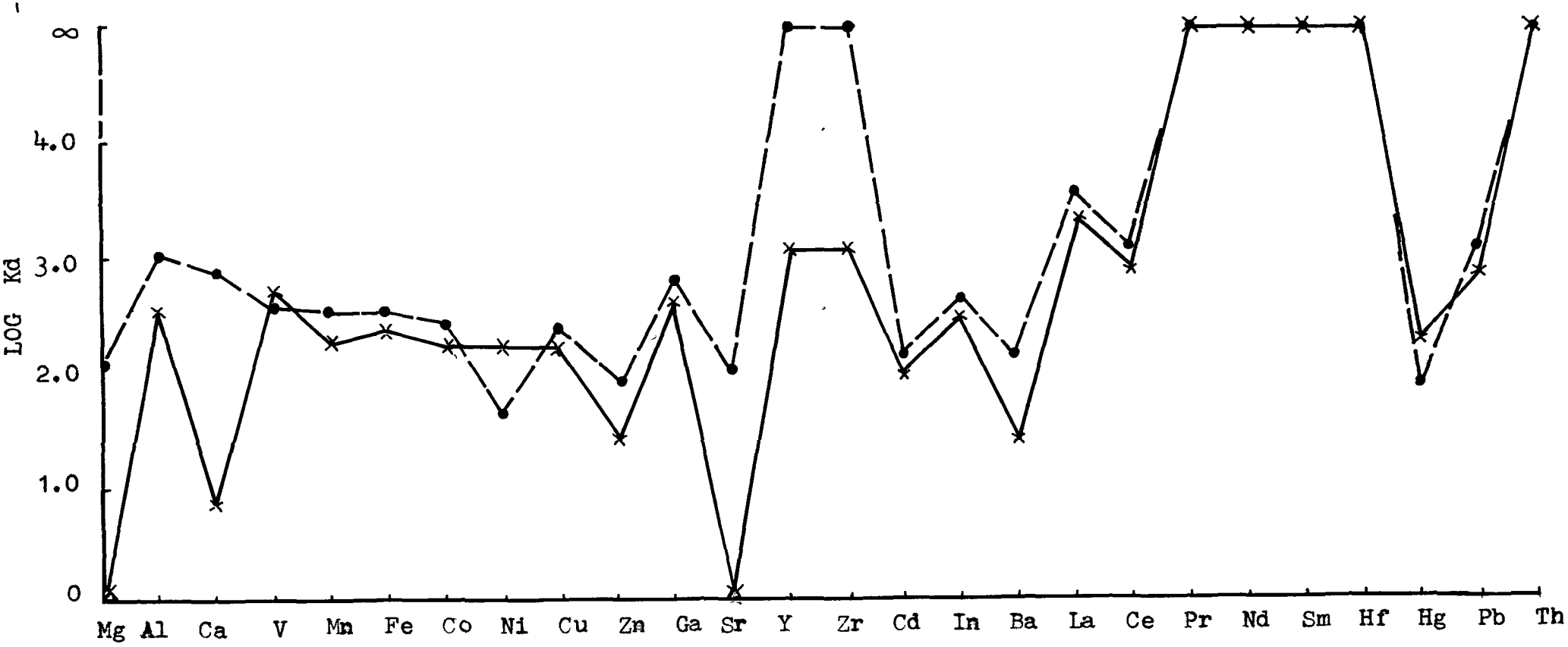



Fig.7 Distribution Coefficients of Metal Ions On Titanium Antimonates.

-x- 0.1M $HNO_3$ + Acetone (9:1)

-●- 0.1M $HNO_3$ + Acetone (1:9)

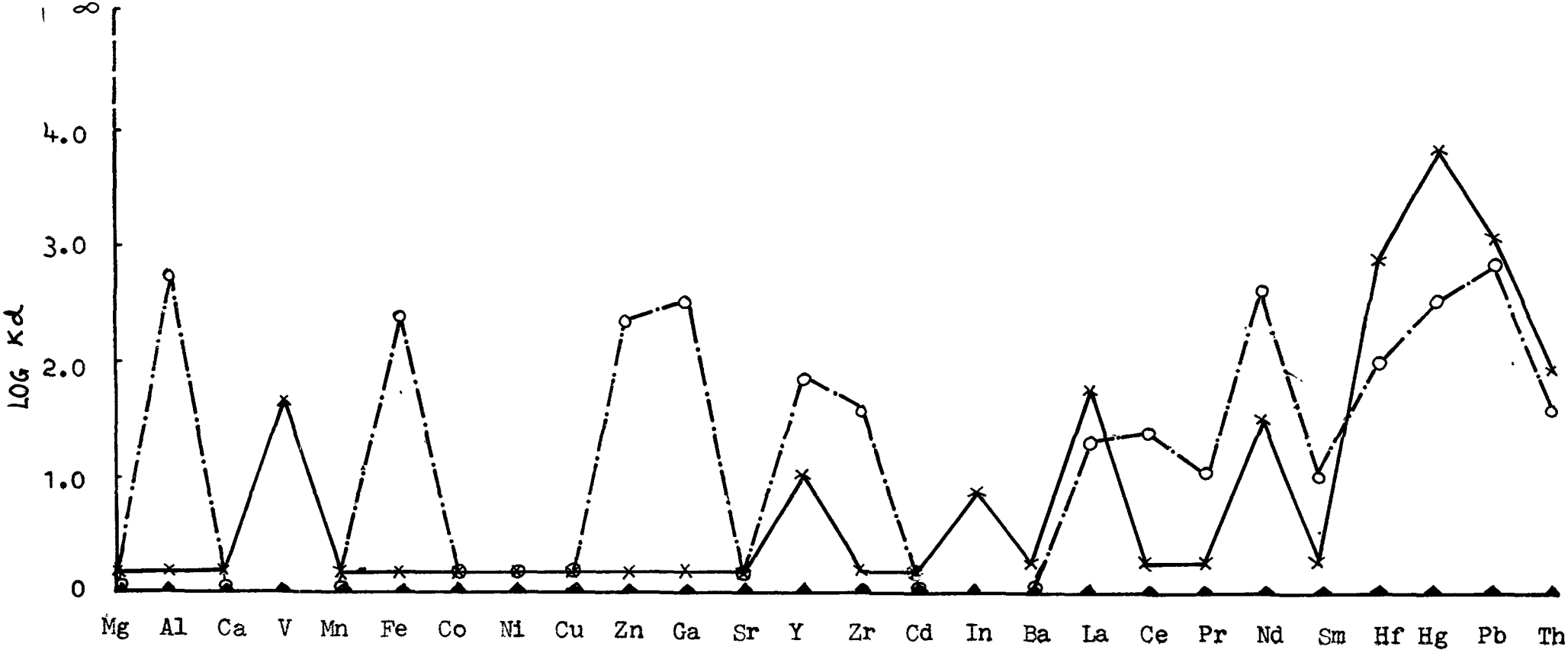



Fig.8 Distribution Coefficients of Metal Ions On Titanium tungstate

-▲- 0.1M $HNO_3$

-o- 0.1M HCOOH

-x- 0.1M $NH_4NO_3$

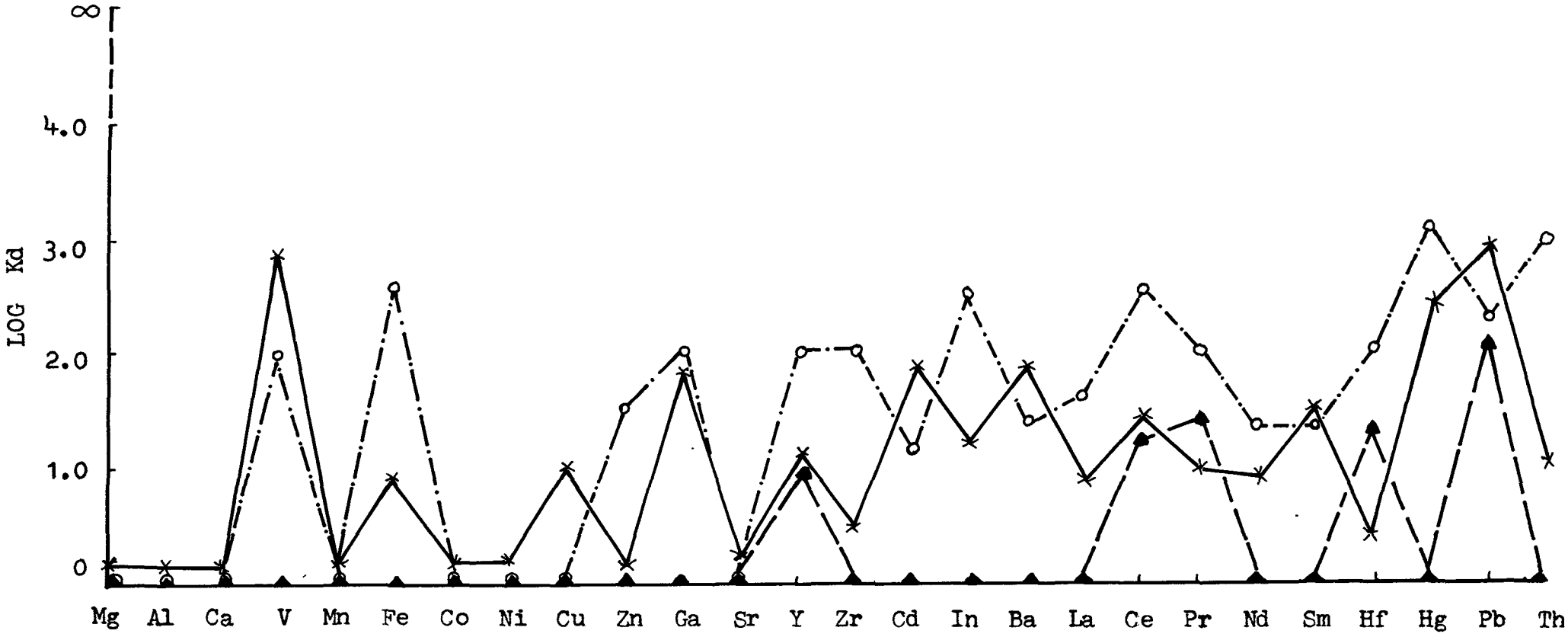



Fig.9 Distribution Coefficients of Metal Ions On Titanium Selenite

-o- 0.1M HCOOH

-x- 0.1M $NH_4NO_3$

-▲- 0.1M $HNO_3$

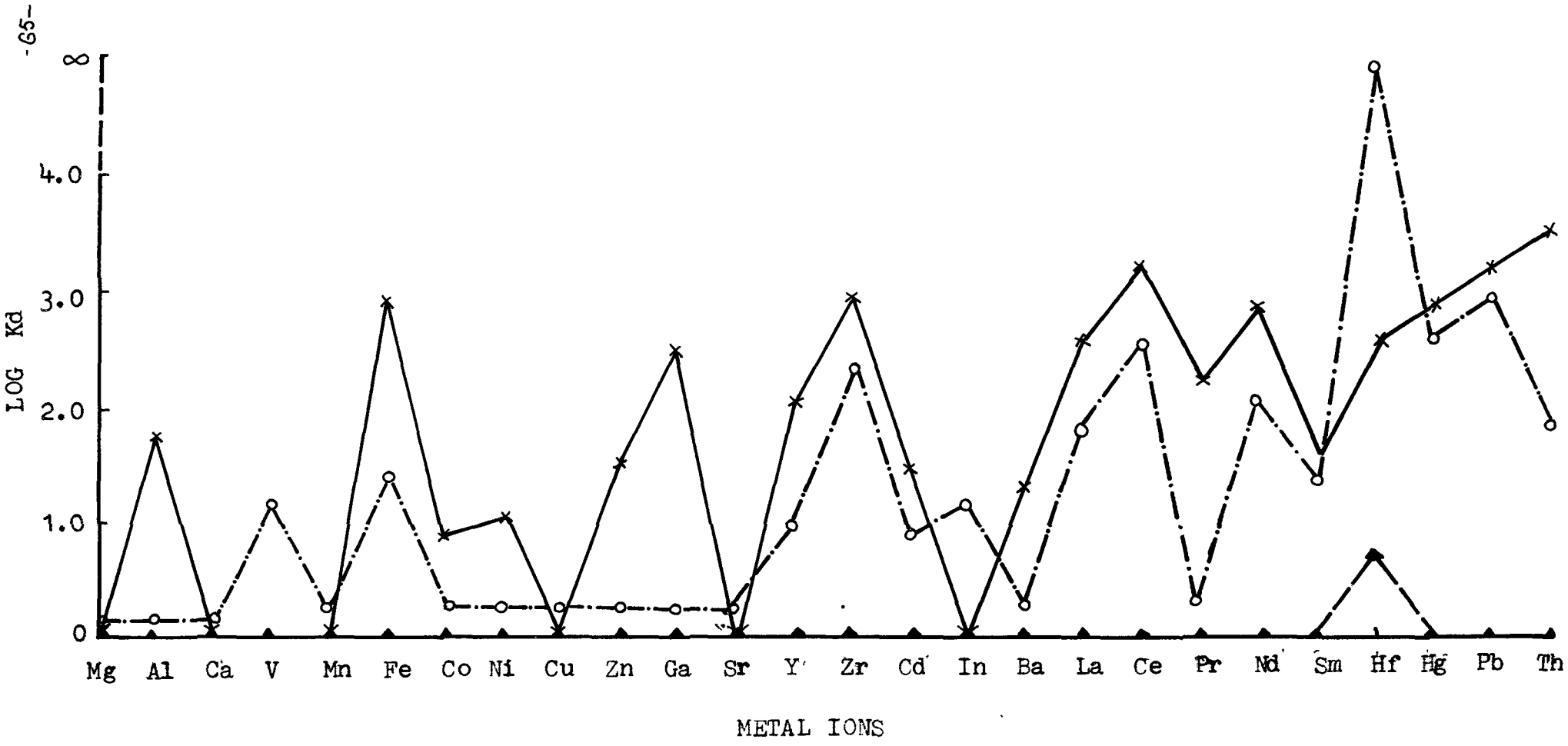



Fig.10 Distribution Coefficients of Metal Ions On Titanium Arsenate

-x- 0.1M HCOOH

-o- 0.1M $NH_4NO_3$

-▲- 0.1M $HNO_3$

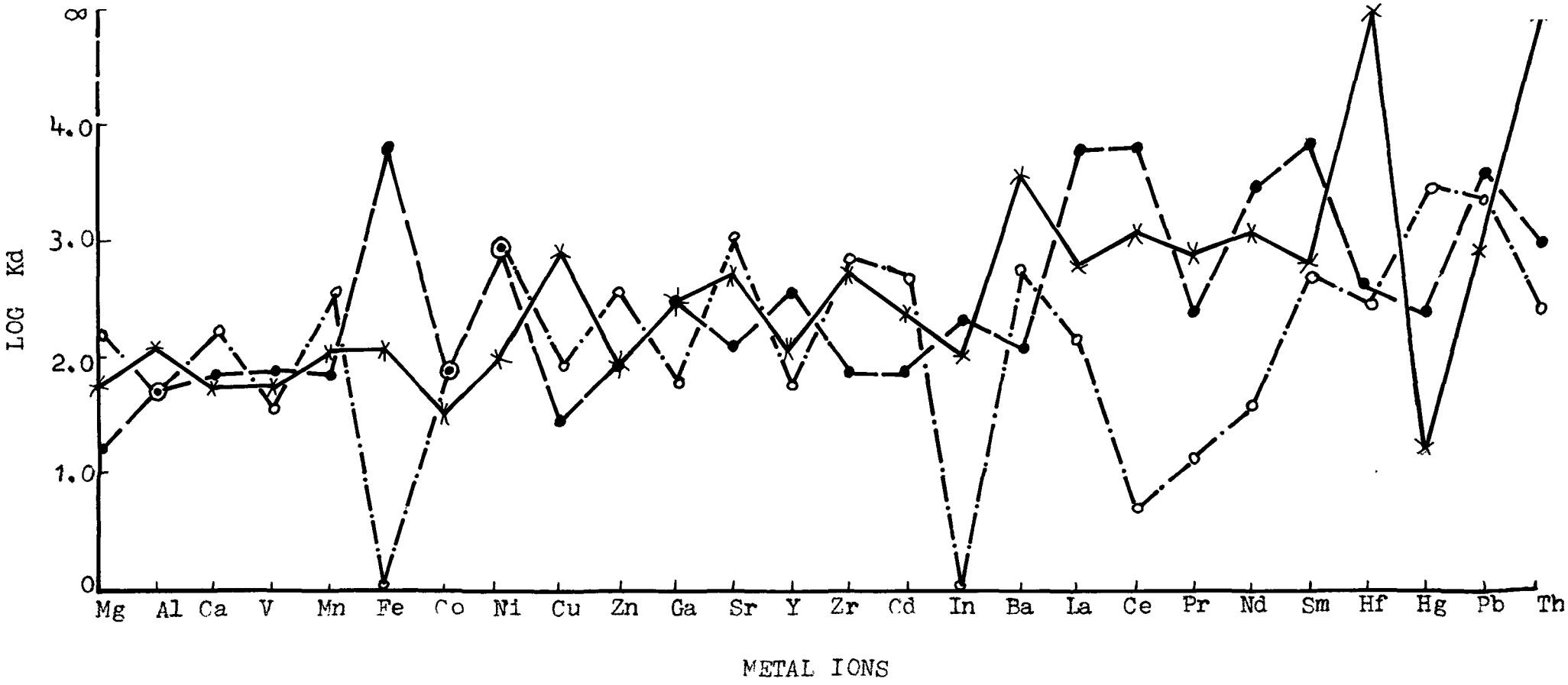



Fig.11 Distribution Coefficients of Metal Ions in Water

-●- Titanium Arsenate

-o- Titanium Tungstate

-x- Titanium Selenite

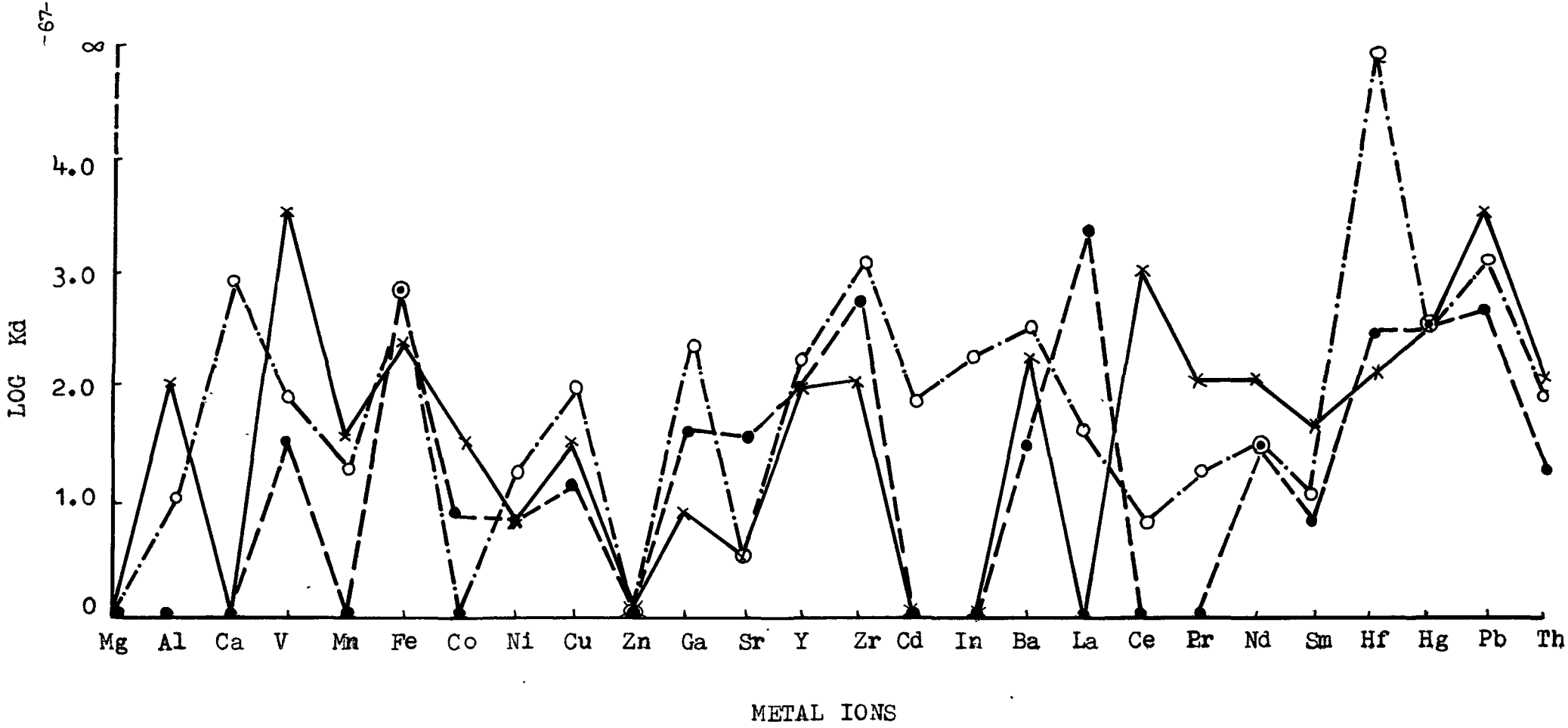
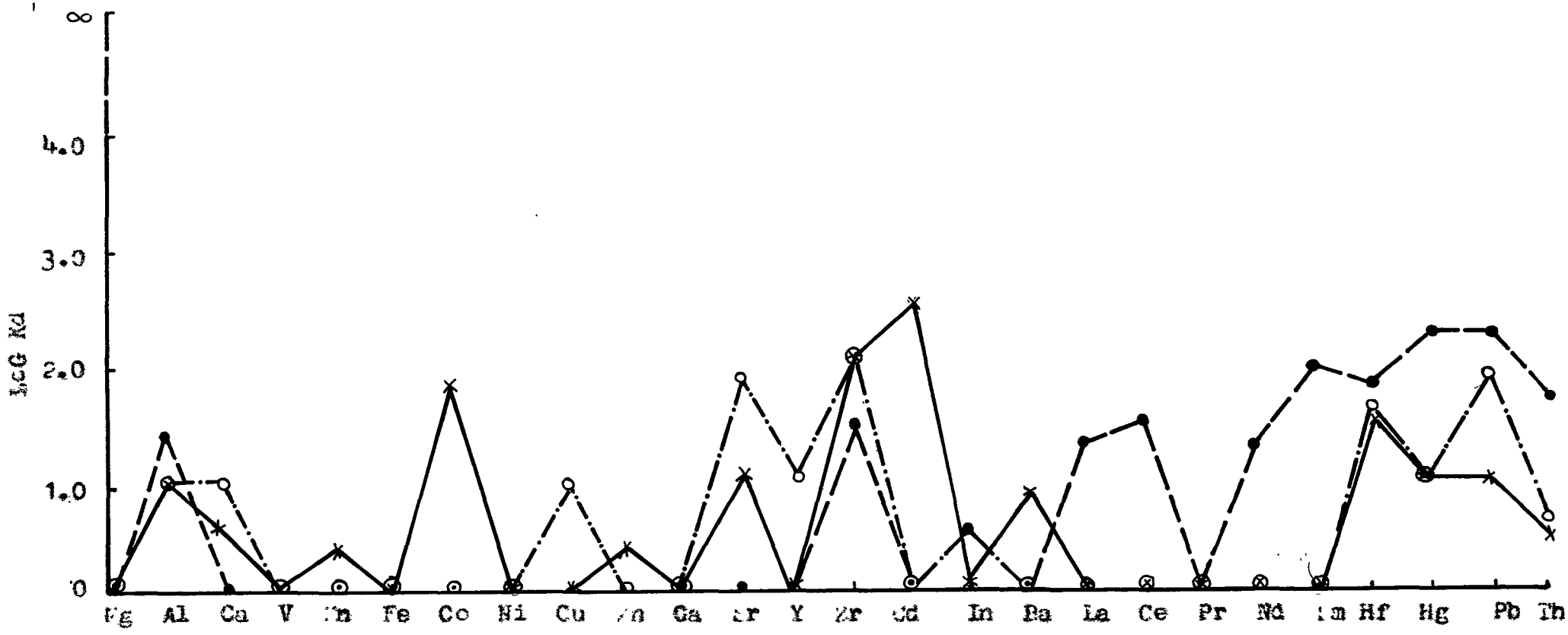



Fig.12 Distribution Coefficients of Metal Ions in Acetone + 0.1M $HNO_3$ (9:1)

-x- Titanium arsenate

-o- Titanium selenite

-●- Titanium Tungstate




METAL IONS

Fig.13 Distribution Coefficients of Metal Ions in 0.01M $HNO_3$

-x- Titanium tungstate

-O- Titanium selenite

-●- Titanium arsenate

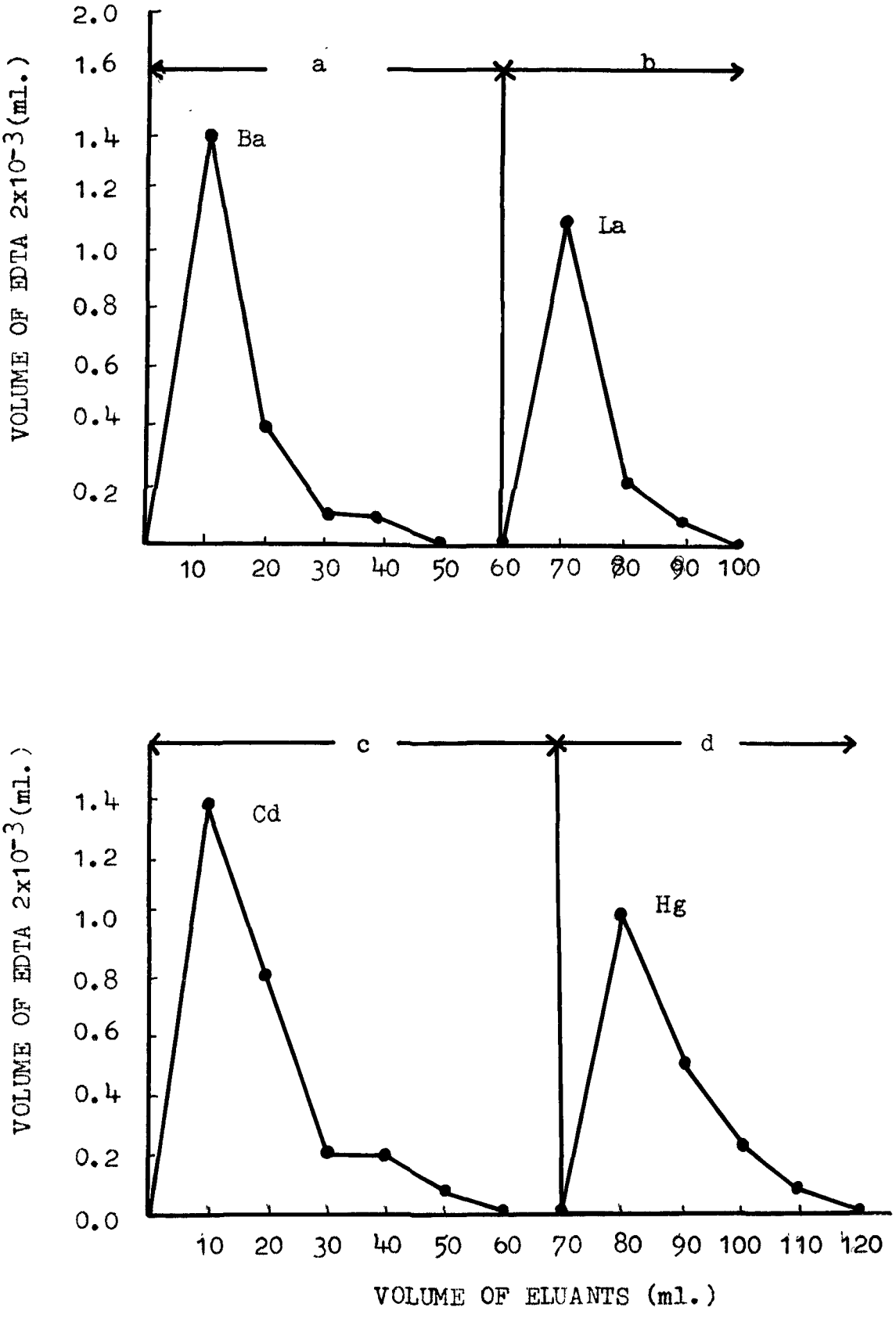



Fig. 14 Separations of Ba from La(III) on Titanium arsenate column and Cd from Hg(II) on titanium tungstate column.

a. Acetone + 0.1M $HNO_3$ (9:1)
b. 2M $HNO_3$
c. 0.1M $NH_4NO_3$
d. 1M $HNO_3$

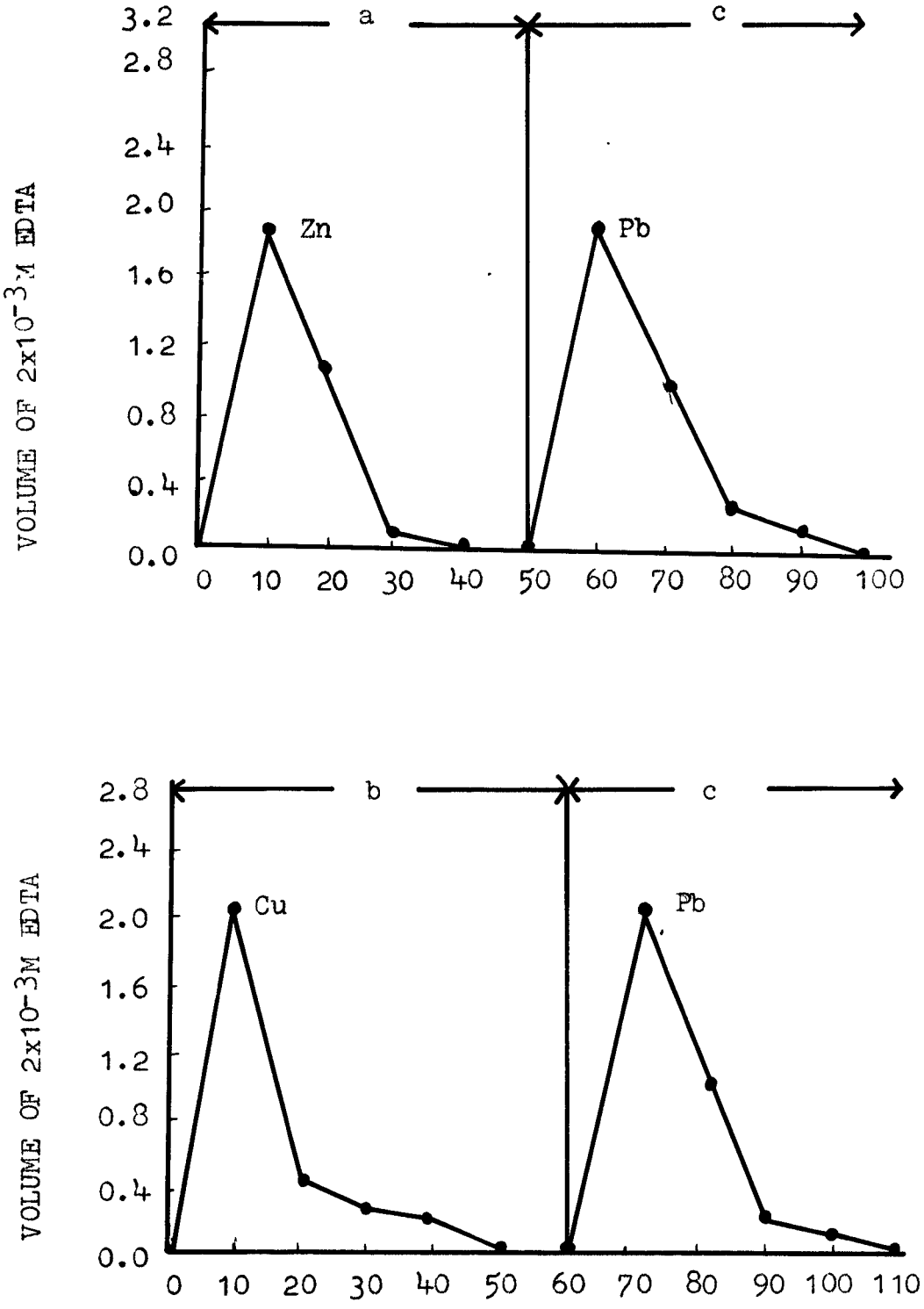



Fig.15 Separation of Zn(II) from Pb(II)
and
Separation of Cu(II) from Pb(II)
On Titanium Tungstate Columns

a. Acetone + 0.1M $HNO_3$ (9:1)
b. 0.1M HCOOH
c. 0.1M $HNO_3$

## DISCUSSION

As a result of this study a number of interesting generalisations can be made, which can help in the selection of the proper exchanger. A comparison of the chemical stability of the various ion exchangers is given in Fig. 1. It is apparent from this figure that titanium molybdate is the least stable and titanium tungstate is the most stable. Therefore we have not used titanium molybdate in our future studies.

It is clear from Fig. 2 that titanium arsenate has the highest ion exchange capacity, and therefore if we are interested in exchangers of high capacities we should chose the arsenates. It will be interesting to compare the ion exchange capacity of the corresponding salts of tin, zirconium and other metal ions also.

The thermal stabilities of the various ion exchangers are compared in Fig 3, and it is apparent that titanium antimonate has the highest thermal stability. Even at 500$^{0}$, it has sufficient ion exchange capacity to be of use an ion exchange material.

A comparison of the Kd values of metal ions on these exchangers in distilled water shows some outstanding features. Thus the antimonate has the highest Kd values of all the four exchange materials studies. This is because the amorphous antimony

oxide has the larger member of the free oxygen sites, where the metal ions can be adsorbed. Therefore the antimonate can be of use only at low pH values, where it can be distinguished between various ions. The tungstate arsenate and selenite on the other hand show high selectivities even in the neutral medium. In the case of the tungstate the Kd values vary from 3300 for Hg(II) to zero for In(III) and Fe(III). This is a characteristic feature of titanium tungstate because all the other exchanger have a very high affinity for Fe(III). In the case of arsenate the highest Kd value is for Pb(II), which shows high Kd values on almost all the exchangers. The lanthanides have the lowest Kd values on titanium tungstate while their highest Kd values are on titanium antimonate as expected.

When the hydrogen ion concentration is raised from $10^{-7}$ to $10^{-2}$ most of the cations have almost zero. Kd values on all the exchangers except on antimonate. At this pH Al(III), Zr(IV), Hf(IV), Th(IV), La(III), Ce(IV) and Sm(III) have Kd values more than 1000. Therefore this exchanger can be used for the following interesting separations.

(1) Al(III) from Ga(III), In(III).

(2) Al(III) from Zn(II).

(3) Al(III) from Mg(II), Fe(III), Co(II), Ni(II), and Mn(II).

A few important separations which may be achieved on titanium tungstate in 0.01M nitric acid are:

(1) Cd(II) from numerous metal ions including Zn(II).

(2) Zr(IV) from numerous metal ions including Hf(IV).

Zr(IV) can also be separated from (IV) on titanium selenite in 0.01M $HNO_3$. In 0.1M nitric acid almost all the ions have zero Kd values except Zr(IV), Hf(IV), and Th(IV) which show complete adsorption even at this pH. Therefore these ions can be separated from numerous metal ions on titanium antimonate columns.

A comparison of the Kd values in acetone and acetone-nitric acid systems on titanium antimonate is very interesting. If we replace 100% acetone with a solution which is 50% in acetone and 0.05M nitric acid then there is a very little difference between the Kd values in the two systems for almost all the metal ions (compare curves 1 & 2 Fig. 6). If however, the nitric acid concentration is increased from 0.05M to 2M nitric acid then there is a significant difference. Now the 26 metal ions are divided into two parts.

(1) Those which have almost zero Kd values, i.e. Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Mn(II), Y(III), Co(IV) and La(III).

(2) The rest which have very high Kd values.

Then one of the ions in the first group can be separated from any one or a group of ions in second group. Some examples are given below:

(a) Hg(II) from Cd(II), Zn(II), Ba(II), Sr(II), Mg(II) and Mn(II).

(b) Ce(IV) or La(III) from Zr(IV), Hf(IV), Th(IV), Pr(III), Nd(III), and Sm(III).

A comparison of acetone + 0.1M in 1:9 and 9:1 ratios (Fig. 7) shows that there is not much difference in the Kd values for most ions except Mg(II), Ca(II) and Sr(II). However, the selectivity sequence is altered for the group Mg(II), Ca(II), Sr(II) and Ba(II). Thus in water we have

$$Ba > Sr > Mg > Ca$$

while in these two systems the sequence is

$$Ba > Ca > Sr = Mg$$

0.1M ammonium nitrate is specially useful because in this solvent system large differences in Kd values are noticed for similar ions. Thus Sm, Nd, and Pr can be separated on titanium arsenate columns. Similarly Ba can be separated from Sr, and Ca can be separated from Zn(II) on the titanium selenite columns. The difficult separation of Zr(IV) and Hf(IV) can be achieved on the titanium tungstate columns. There are a large number of possibilities which exist for difficult analytical separations. These are summarized in Table XVI.

TABLE - XVI

Possible separations on Titanium based exchangers

| Exchanger \ Solvent | 0.1M $HNO_3$ | 0.1M $NH_4NO_3$ | 0.1M HCOOH |
|---|---|---|---|
| Titanium antimonate | Mg - Ba<br>Zn - Hg<br>Ga - Al, In<br>Pb - Cu, Fe, Mn, Co, Ni, V, Zn and Mg. | Mg - Zn,Sr,Cd, Pb,Al,In,Ga,V, and rare earths. | - |
| Titanium arsenate | - | Zn - Hg, La, Zr, Ce and Hf.<br>Al - Hg<br>Pb - Ga<br>Pb - Mn, Mg, Ca, Ba. | Ca - La,Ba,Hg.<br>Mg - Al<br>In - Ga<br>V - Pb<br>Mn - Pb<br>Cu - Fe<br>Hg - V, Mn |
| Titanium selenite | Hf - La, Zr,Th, Nd and Sm.<br>Pr - Nd,Sm and La.<br>Fe - Cu,Mn,Co, Ni, In.<br>Al - Hg. | Ba - Ca, Mg,Sr,<br>Zn - Cd and Hg.<br>Pb - Ni,Co,Mn<br>Al - Ga<br>V - Ni and Co. | Ba - Mg-Ca,Sr.<br>Al - In,Ga<br>Fe - In |
| Titanium tungstate | - | V - Mn<br>Hg - Cd,Al,Cu Ga,Fe,Co and Ni<br>Pb - Cd,Al,Ga, Fe,Cu,Co and Ni. | Zn - Mg,Ba,Sr Ca and Cd<br>Fe - Cu,Co,Ni, Mn and In<br>In - Ga, and Al |

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# C H A P T E R - V

## MICRO-DETERMINATION OF BROMATE IONS WITH ANTIPYRINE

Antipyrine is an important derivative of 5-pyrazalone class and it is used for the detection and determination of a number of compounds[1]. It is tautomeric in nature and its most stable state is the keto form in which most of the reactions occur. A few reactions have been quoted in the literature, which are due to the enolic form[2].

Very few methods are available for the determination of bromate ions[3-7]. The method described by Macdonald and Yoe[3] is not suitable, because, the color is unstable and a large number of inorganic ions interfere. The method of Hashmi[5] is long and tedious. An effort was therefore made to develop a fast and selective method for the determination of bromate ions. A new method is now proposed based on the formation of a red colored product which is obtained by the interaction of antipyrine, sodium nitrite, perchloric acid and bromate ions.

## EXPERIMENTAL AND RESULTS

Reagents: All the reagents were of Analytical grade or comparable purity.

A 5% W/V aqueous solution of antipyrine (from Rhodia, France). 0.1M Sodium nitrite solution.

Apparatus: Bausch and Lomb "Spectronic 20" spectrophotometer was used for absorbance measurements.

Standard Solution of Bromate: This was prepared by dissolving 16.70 g of potassium bromate in distilled water and diluting to 1000 ml. The solution contained $125 \times 10^2$ µg/ml of bromate ions. More dilute solutions were prepared by diluting the stock solution with water.

Procedure for Determination of Bromate: To 3 ml of the 5% antipyrine solution were taken in a 12 cm. long test tube, are added 3 ml of 60% perchloric acid and 1 ml of 0.1M sodium nitrite solution. The contents are air cooled to room temperature and transferred to a 10 ml volumetric flask. Samples having a concentration range of 25.0 - 140.0 µg/ml of bromate ions are added.

The solution is made up to the mark with distilled water and well mixed. The absorbance was taken against the blank at 525 mμ.

Absorption Spectra: The absorption spectrum of the solution containing 80.6 μg of bromate ions was taken against a reagent blank. The maximum absorption occurred at 525 m μ (see Fig. 16). The spectrum of the reagent blank against distilled water was also taken (see same figure).

Effect of Variation in the Amount of the Reagents: Several experiments were carried out by varying the amount of one reagent and keeping constant the amount of the other reagents. This resulted in a change in absorbance. In all the three experiments the amount of bromate ion taken was 102.4 μg. First of all identical aliquotes of 3 ml of 60% perchloric acid, 1 ml of 0.1M sodium nitrite were added seperately in 1.0, 3.0, 3.0 and 4 ml of 5% antipyrine solution. The four sample solutions were diluted with water upto the mark. The absorbance of the sample solution containing 4 ml of antipyrine was found to be maximum. However, the color existed for 15 minutes and then become turbid, either due to the precipitation of the excess antipyrine or due to insufficient amount of perchloric acid. The maximum absorbance was obtained in sample solution containing 2 ml of perchloric acid. The disadvantage in this system was that the color was stable for only 30 minutes. Moreover it was found that antipyrine

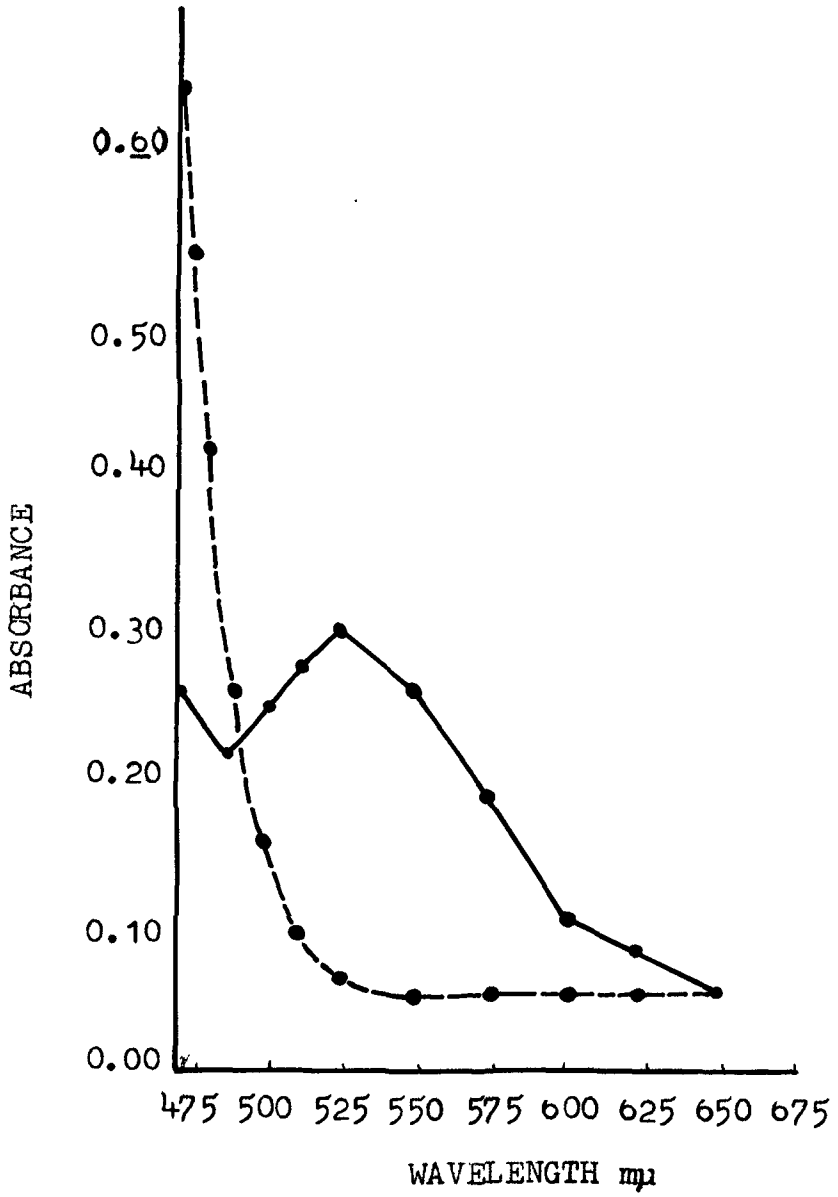



Fig.16 Absorption Spectrum

-●-89.6 μg Bromate ions Vs. Reagent Blank

--o-- Reagent Blank Vs. Water

was precipitated when the amount of perchloric acid was less than 1.5 ml and became unstable when the amount was more than 3 ml. Finally 3 ml of 5% antipyrine and 3 ml of 60% perchloric acid were added in 2.0, 1.5, 1.0 and 0.50 ml of 0.1M $NaNO_2$. The maximum absorbance was found in sample solution containing 1.0 ml of sodium nitrite. This system was found to be the most appropriate. A study of time versus absorbance was carried out which showed that the color of the complex was stable for 1.5 hours.

Conformity with Beer's Law: The absorbance measurements of bromate ions were made at 523 mu. It was found that Beer's Law is obeyed for solutions containing 25.0 - 140.0 µg/ml of bromate. Sensitivity as defined by Sandell[8] was found to be 0.029 $BrO_3^-/cm^2$ for $\log {}^{I_o}/_{I} = 0.04$ with a molar absorptivity $2 \times 10^3$ $mole^{-1}$ $cm^{-1}$ liter.

Effects of Diverse Ions in Bromate Determination: To a solution containing 128 µg/ml of bromate ions the following ions were added and it was found that 15-fold excess caused no interference. Al(III), Ba(II), Be(II), Bi(III), Cu(II), Cr(III), Ca(II), Co(II), Ga(III), Au(III), Hf(IV), In(III), Li(I), La(III), Pb(II), Mn(II), $Hg_2$(II), Ni(II), K(I), Na(I), Ag(I), Sr(II), Th(IV), Tl(I), Y(III), $NO_3^-$, $SO_4^{-2}$, $I^-$ and $Br^-$.

The following ions were found to interfere but they were tolerated upto the amount (µg) indicated in parenthesis As(III)(75),

Ce(IV)(7), Fe(III)(11.2), $Cl^-$(71), $CrO_4^{-2}$(11.5), $Cr_2O_7^{-2}$(108).

Unknowns were run to see the validity of the method and the results are given in Table XVII.

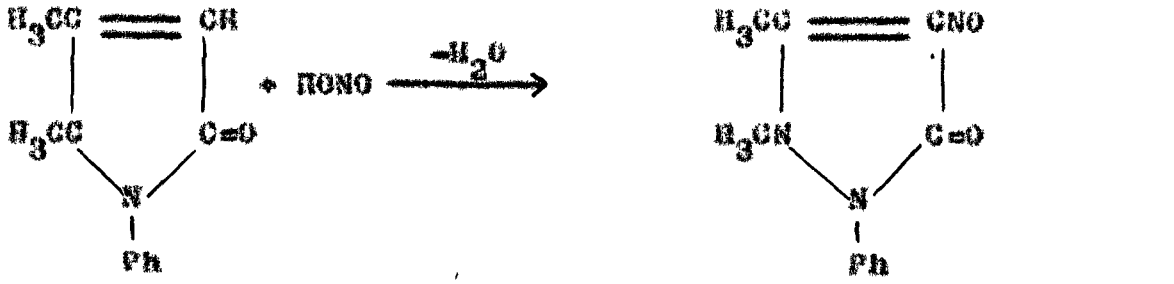
TABLE - XVII

Determination of bromate ions in the given unknown samples

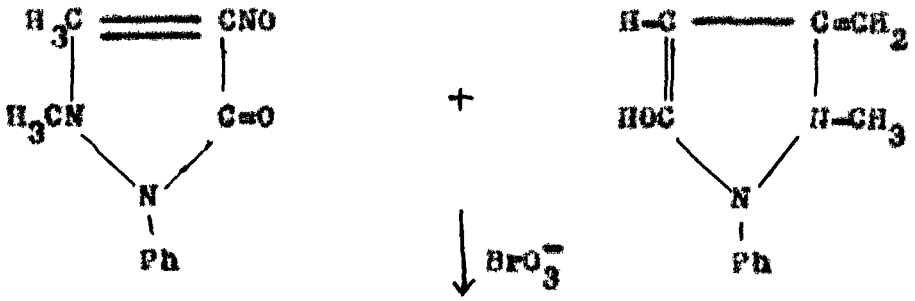
| No. | $BrO_3^-$ given µg/10 ml. | $BrO_3^-$ found µg/10 ml | % Error |
|---|---|---|---|
| 1. | 89.6 | 89.0 | - 0.6 |
| 2. | 76.8 | 76.0 | - 1.0 |
| 3. | 115.0 | 115.2 | + 0.2 |
| 4. | 76.0 | 76.0 | ± 0.00 |
| 5. | 99.0 | 100.0 | + 1.00 |
| 6. | 128.0 | 126.0 | - 2.00 |
| 7. | 99.0 | 100.0 | + 1.00 |
| 8. | 76.8 | 76.0 | - 1.00 |
| 9. | 102.0 | 100.0 | - 2.00 |
| 10. | 115.0 | 115.2 | + 0.20 |

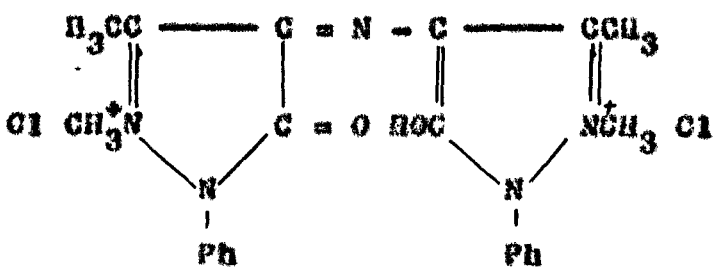
## DISCUSSION

Antipyrine reacts with sodium nitrite in presence of an acid and produce 4-nitrosoantipyrine which is light blue or green in dilute solution. The colour change from green to red is due to the formation of Antipyrine red[9]. The mechanism of this reaction is postulated as follows:




(Green) 4-nitrosoantipyrine




(Antipyrine red)

The ions such as As(III), Ce(IV), Fe(III), $CrO_4^{-2}$ $Cr_2O_7^{-2}$ and $Cl^-$ interfere in the determination.

If perchloric acid is replaced by acetic acid then the bromate ions give a violet colour with antipyrine and nitrous acid. This is a specific colour reaction which is not given by any other ion except the bromate ion. Finally in acetic acid medium the bromate ions give a very light pink colour. This appears to be a useful test for bromate ions with no interferences either from chlorate or nitrate ions.

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# C H A P T E R - VI

## PAPER CHROMATOGRAPHY ON STANNIC ANTIMONATE PAPERS.

Chromatography on papers impregnated with inorganic ion exchangers of the type zirconium phosphate have been recently reviewed[1]. Some interesting possibilities for the separation of alkaloids and amino acids on zirconium phosphate papers have also been reported[2]. In the earlier reports[3-6] from this laboratory it was observed that these papers are highly selective and they give rapid separations with simple aqueous systems. The selectivity of these papers is greatly enhanced if mixed solvent systems are used in place of aqueous systems[7]. Some important quantitative separations have also been achieved[8].

These studies on ion exchange papers have the following limitations.

1. No systematic studies in nitric acid systems have been reported. Sastri[9] used 3.0N nitric acid to separate U(IV) from U(V), 1.0N nitric acid to separate As(III) from As(V) and 0.1M nitric acid to separate Hg(I) from Hg(II). Zhang Zhu[10] separated Y(III) from Sr(II) using 0.1M to 2.0M nitric acid solutions.

2. Rf values on treated and untreated papers using acids of

the same concentration as eluents have not been studied.

The present work was therefore undertaken to make a systematic study of the behaviour of numerous metal ions on stannic antimonate papers. It had been reported earlier by Kraus[11] that zirconium antimonate is specific for sodium ions and therefore Alberti[1] had predicted that zirconium antimonate papers should show a high selectivity for $Na^+$ ions. Kraus also observed that zirconium antimonate shows unusual selectivity for alkali metals. We do not have facilities for using radioactive tracers and therefore we could not test the specificity of this material for $Na^+$ ions. However, we have chosen stannic antimonate papers for two reasons.

1. If they show unusual selectivity for the alkali metals they may also exhibit some unusual features with respect to other ions.

2. In our laboratory stannic antimonate has been synthesized[12] and Kd values have been determined on this exchanger. Therefore it will be useful to compare the Kd values and Rf values on this material. The results obtained are summarized in this Chapter.

## EXPERIMENTAL AND RESULTS

Reagents: All the chemicals and solvents were used of either E. Merck (Darmstadt) or B.D.H. AnalaR. Stannic chloride (B & A) and antimony pentachloride of density 2.3 g/ml (B.D.H.) were used.

Apparatus: Chromatography was performed on 15 x 3 cm Whatman No.1 paper strips in 20 x 8 cm glass jars by the ascending method.

Preparation of Ion-Exchange Papers: A 0.25M solution of stannic chloride in distilled water and a 0.25M solution of antimony pentachloride in 4N hydrochloric acid were prepared. Whatman No. 1 strips (15 x 3 cm) were first passed through antimony pentachloride solution for 30 seconds. The excess of the antimony pentachloride was removed by placing the strips on a filter paper sheet. The strips were then dipped in stannic chloride solution for 30 second and the excess was then drained off. The strips were dried at room temperature over-night, washed three times with distilled water in order to remove the excess reagent, and were finally allowed to dry at room temperature for 12 hrs. and were used as such.

Cation solutions: 0.1M solutions of chlorides, nitrates, or sulphates of most of the cations were prepared in 0.1M solution of the corresponding acids. Bismuth was prepared in 30% (V/V) hydrochloric acid solution. One percent solutions of gold and gallium chlorides were prepared in 4M hydrochloric acid and niobium pentachloride (1%) was prepared in 10% tartaric acid. Selenium dioxide was dissolved in water and made alkaline with 1N KOH solution. Ceric sulphate was prepared in 3N sulphuric acid, mercuric nitrate solution was prepared in 0.5N nitric acid, $As_2O_3$ and $Be(NO_3)_2$ were dissolved in 1% nitric acid.

The valencies of the metal ions used are as follows unless otherwise stated. Be(II), Mg(II), Al(III), K(I), Ca(II), Ti(IV), V(IV), Cr(III), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Ga(III), As(III), Se(IV), Rb(I), Sr(II), Y(III), Zr(IV), Nb(V), Mo(VI), Ru(III), Pd(II), Ag(I), Cd(II), In(III), Cs(I), Ba(II), La(III), Ce(III), Pr(III), Nd(III), Sm(III), Hf(IV), Ir(IV), Pt(VI), Hg(II), Tl(I), Pb(II), Bi(III), Th(IV), $UO_2$(II), Au(III), (W)(VI).

Detector: Saturated $H_2S$ solution was used to detect Ag, Pb, Cu, Bi, Hg, Tl, Cd, As, and Pd. A fresh solution of sodium cobaltinitrite was used to detect K , Rb, Cs. A 1% solution of Alizarine Red S was used to detect La, Ce, Ce(IV), Y, Zr, Th, Hf, In, Ca, Nb, Pr, Sm and Nd. Stannous chloride in hydrochloric acid was used to detect Au, Pt, Mo, Se, and W; Al, Be and Ga were detected by

1% alcoholic solution of aluminon. Diphenyl carbazide was used to detect Mn, Cr, Ir and Zn; Fe(III), V, $UO_2$ were detected with potassium ferrocyanide and Fe(II) with potassium ferricyanide. Mg was detected with quinalizarine. A fresh 5% solution of sodium rhodizonate was used to detect Ba and Sr; Ru was detected with 2N hydrochloric acid solution of thiourea.

Procedure: Thin glass capillaries were used to apply the test solution on papers. The chromatograms were conditioned for 5 to 10 minutes and then the solvent was allowed to ascend, 11 cm from the starting line. To obtained a clear picture of the size of the spot, instead of simply giving Rf values of the spots. The Rf of the front limit (RL) and Rf of the rear limit (RL) of the spots are given in parentheses.

In order to predict and develop separations of analytical importance chromatographic behaviour of metal ions was studied on stannic antimonate papers in the following solvent systems.

1. Different concentrations of nitric acid
2. Nitric acid and ammonium nitrate mixture.
3. Water.

The results are summarized in Fig. 17 - 19. It was found possible to achieve experimentally a number of binary and ternary separations. These are summarized in Table XVIII.

TABLE - XVIII

Some important separations achieved on the stannic antimonate papers.

| Solvents | Separations achieved | Time |
|---|---|---|
| 4M $HNO_3$ | Hf (0.00-0.10) - U (0.60 - 0.80) | 30 minutes |
| | Hf (0.00-0.12) - Nd(0.56-0.86) | " |
| | Hf (0.00-0.10) - Sm(0.65-0.85) | " |
| | Tl (0.00-0.30) - V (0.80-1.0) | " |
| | Mo (0.00-0.10) - V (0.80-1.00) | " |
| | Mo (0.00-0.10) - U (0.50-0.90) | " |
| | Ag (0.00-0.05) - Tl(0.28-0.40) - Cd(0.75-1.00) | " |
| Solvent system 0.1M $HNO_3$ | La (0.00-0.25) - Ca (0.85-1.00) | " |
| | Cd (0.00-0.10) - Hg (0.65-0.90) | " |
| | Ir (0.00-0.05) - Pt (0.80-1.00) | " |
| | W (0.00-0.05) - Pt (0.82-1.00) | " |
| | Al (0.20-0.38) - Cr (0.90-1.00) | " |
| | Ba (0.30-0.55) - Ca (0.90-1.00) | " |
| | Sr (0.40-0.60) - Ca (0.90-1.00) | " |
| | Mg (0.30-0.40) - Ca (0.90-1.00) | " |
| | Cu (0.18-0.38) - Ca (0.89-1.00) | " |
| | Ag (0.00-0.05) - Ni (0.10-0.38) - Pt (0.75-1.00) | " |
| | Ag (0.00-0.05) - Ni (0.10-0.35) - Hg (0.70-1.00) | |

TABLE-XVIII (Contd.)

| Solvents | Separations achieved | Time |
|---|---|---|
| | Ag (0.00-0.03) - Ni (0.10-0.38) - Pd (0.80-1.00) | 30 minutes |
| | Tl (0.00-0.08) - Be (0.35-0.55) - Ca (0.80-0.95) | " |
| | Cu (0.00-0.20) - Be (0.40-0.60) - Ca (0.90-1.00) | " |
| Solvent system 0.1M $HNO_3$ + 1M $NH_4NO_3$ | Ba (0.40-0.60) - Sr (0.80-0.95) | " |
| | Ag (0.00-0.03) - Au (0.60-0.70) - Hg (0.80-1.00) | " |
| | Fe (0.00-0.05) - Zn (0.12-0.33) - Mn (0.90-1.00) | " |
| | Ag (0.00-0.03) - Au (0.50-0.70) - Pd (0.90-1.00) | " |
| | Ag (0.00-0.03) - Au (0.50-0.70) - Pt (0.90-1.00) | " |
| | Ir (0.00-0.10) - Au (0.50-0.70) - Pt (0.90-1.00) | " |
| | Se (0.00-0.10) - Au (0.55-0.75) - Pt (0.80-1.00) | " |
| Solvent system 1.0M $HNO_3$ | Th (0.00-0.20) - U (0.35-0.75) | " |

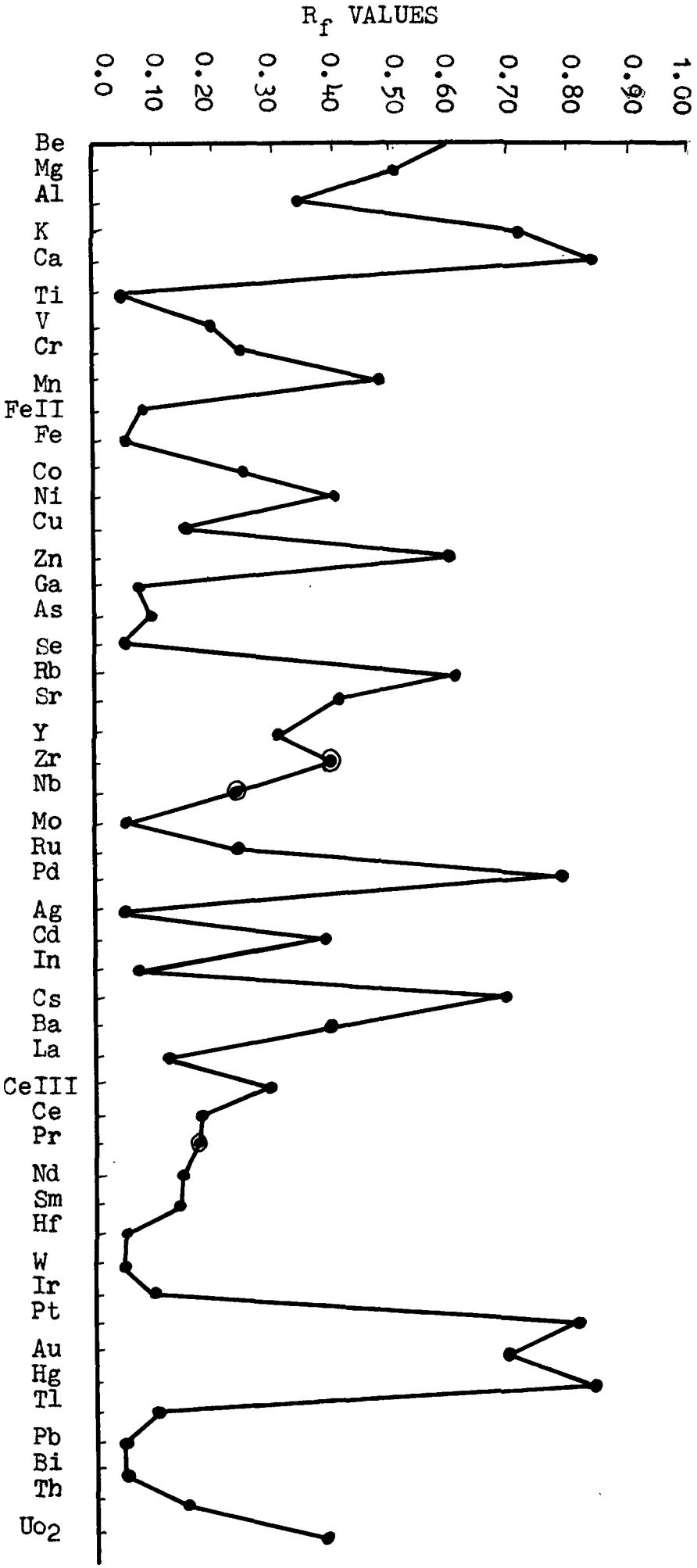



Fig. 17 A plot of $R_f$ Values of 48 Metal Ions useing 0.1M $HNO_3$

◉ Tailing

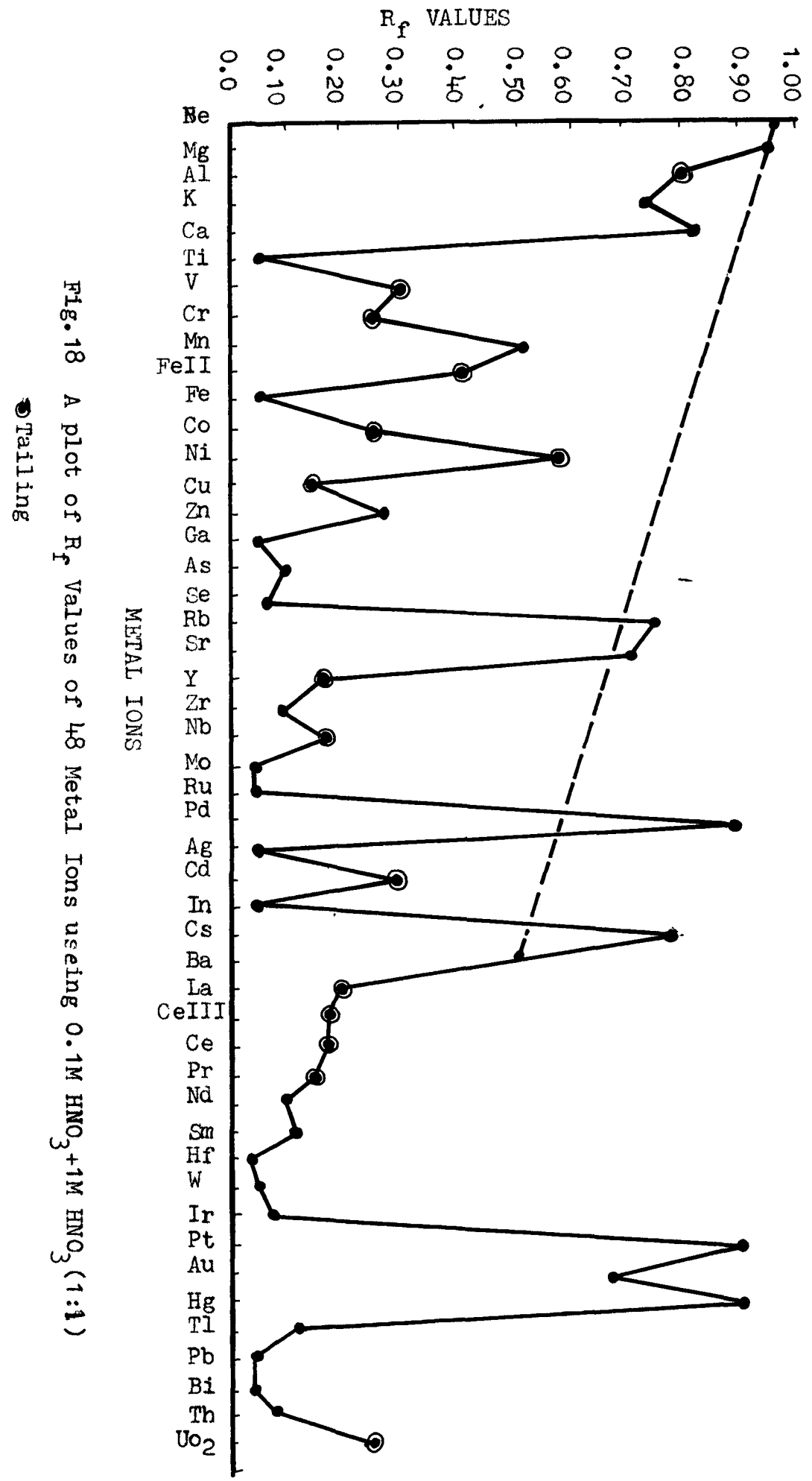



Fig.18 A plot of $R_f$ Values of 48 Metal Ions useing 0.1M $HNO_3$+1M $HNO_3$(1:1)

● Tailing

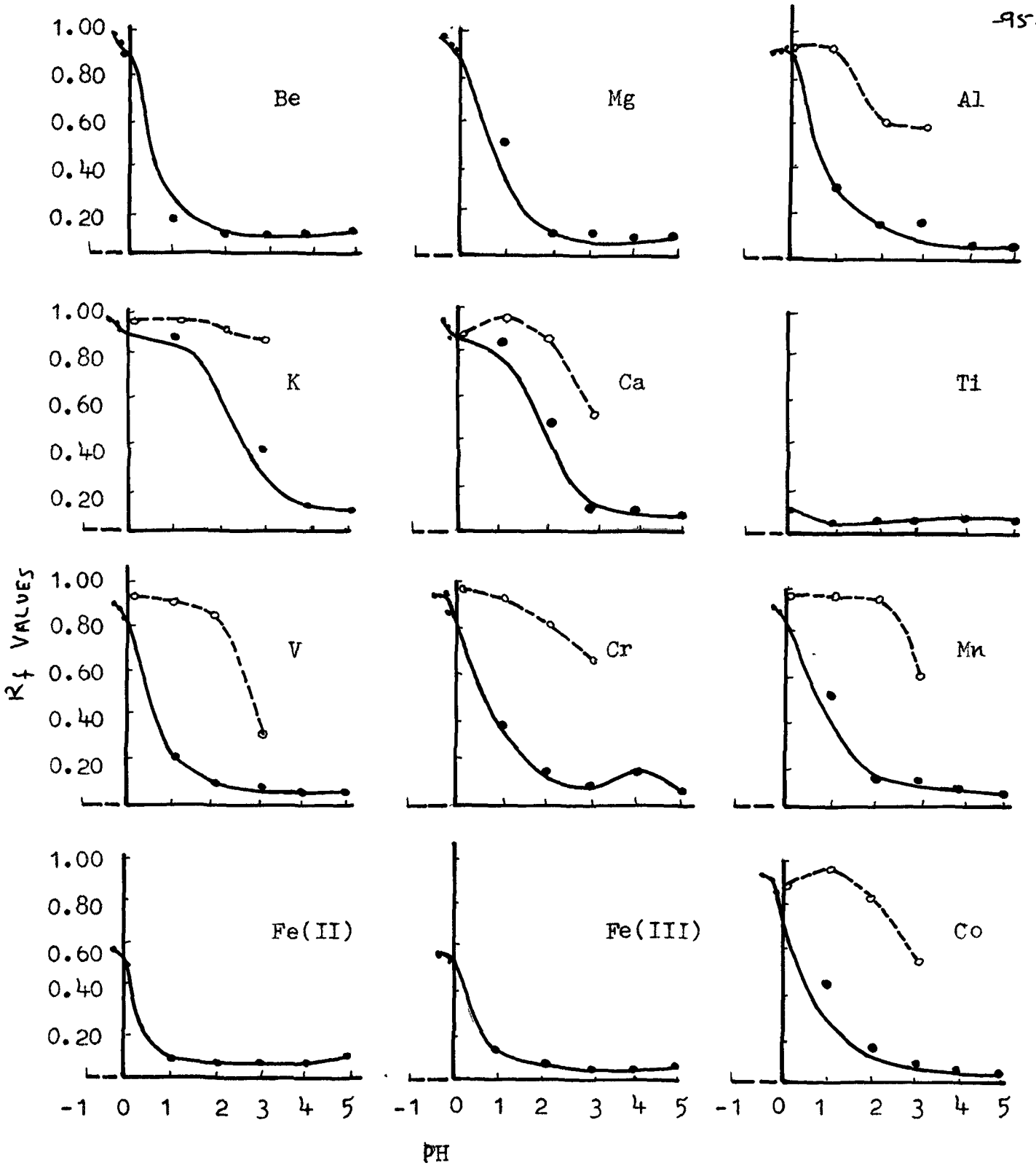
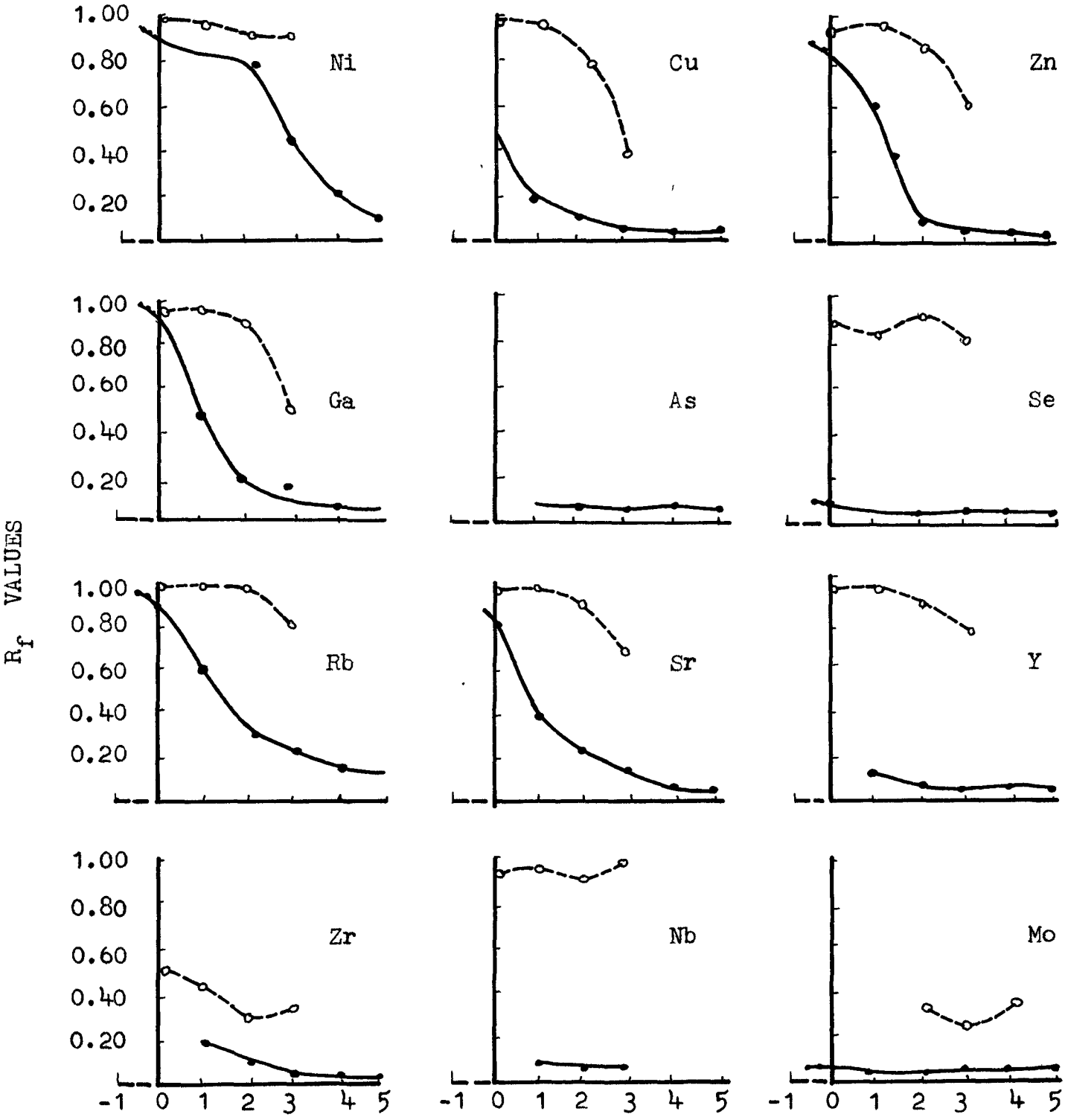


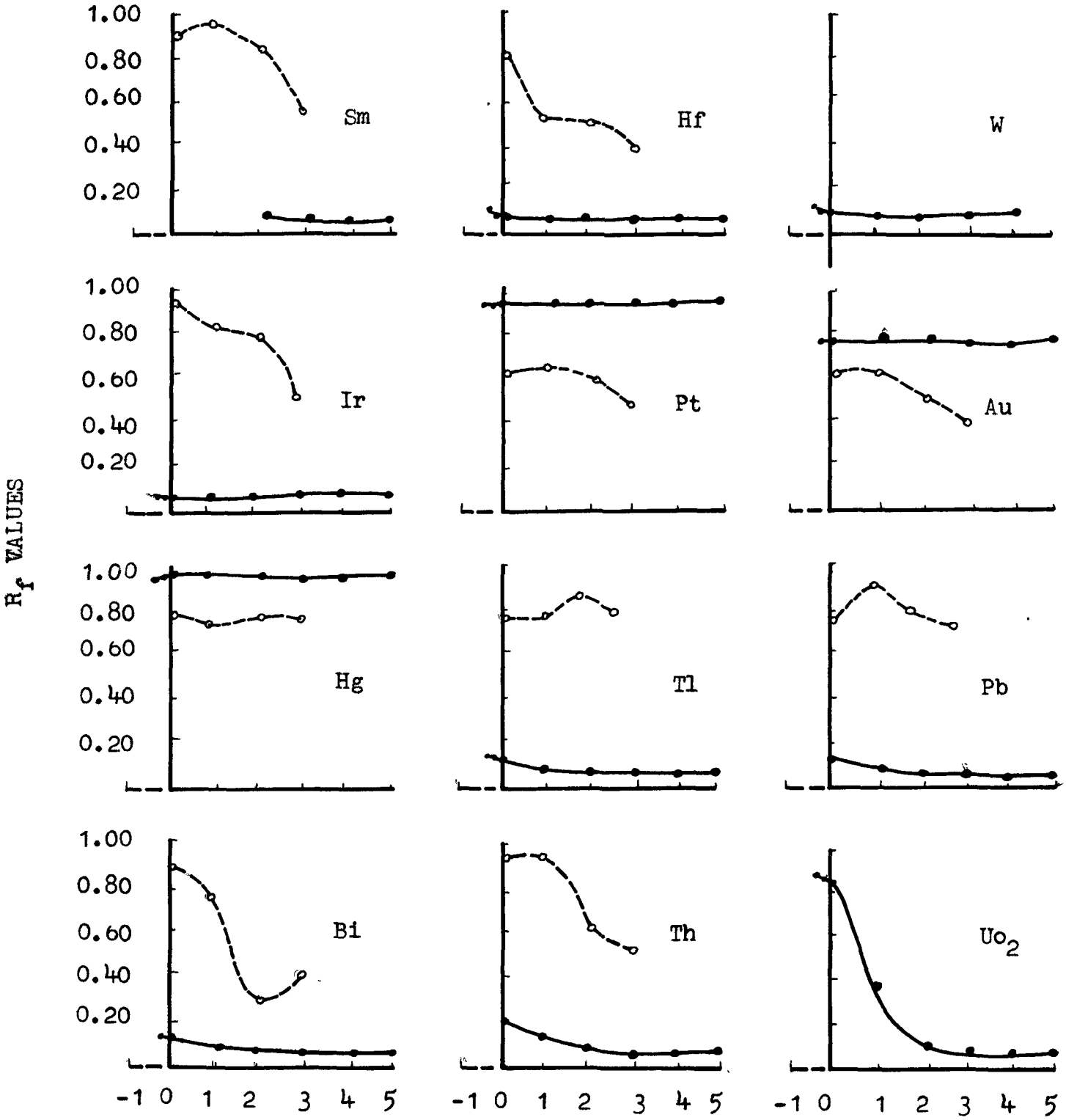

Fig.19 Separation of $R_f$ Values at different PH on paper impregnated with Stannic antimonate and Whatman No.1

.o.. Untreated papers
—•— Treated papers.

continued


1.00
0.80
0.60
0.40
0.20
$R_f$ VALUES
Ni
Cu
Zn
Ga
As
Se
Rb
Sr
Y
Zr
Nb
Mo
-1 0 1 2 3 4 5

continued


$R_f$ VALUES
1.00
0.80
0.60
0.40
0.20
Sm
Hf
W
Ir
Pt
Au
Hg
Tl
Pb
Bi
Th
$Uo_2$
-1 0 1 2 3 4 5

# D I S C U S S I O N

A plot of atomic number vs Rf values in 0.1M nitric acid (Fig. 17) shows some interesting features. A periodicity is observed in this case and maxima and minima occur almost regularly. All the ions on the maxima are either divalent or monovalent except Pt which is negatively charged. All the ions at the minima are either trivalent or have a higher charge except Ag, which probably interacts with the filter paper and has a low Rf value even on untreated papers (Fig. 19) thus this exceptional behaviour become abundantly clear with the help of these plots. Another point worth mentioning is that as the pH increases the Rf values decrease considerably, except in the case of Pd, Pt and Hg. This may also be due to the fact that these species are either positively charged or they are wholly or partly covalent.

Some interesting inferences can be drawn from the plot of Rf values in Fig. 18. In this case the solvent is 0.05M in nitric acid and 0.5M in ammonium nitrate. Therefore there should be a decrease in Rf values both due to a decrease in the hydrogen ion concentration and due to an increase in the ionic strength. However in the case of Be, Mg and Al there is an increase in the Rf value, which may be due to complex formation with ammonium ions.

As one goes from Be to Ba there is a decrease in Rf values and all the Rf values of the metal ions in Hind, A group of the periodic table lie in one straight line. This is due to the fact that as the ionic radii increases the hydrated radii decreases and therefore ions with small ionic radii have large Rf values and vice versa. The other factors on which ion exchange depends, i.e., the charge and the ionic matrix interaction are probably the same for all these ions.

A plot of pH vs Rf values on treated and untreated papers is very instructive. If we consider the simple monovalent $K^+$ ion which does not form many complexes than we can see that the stannic antimonate acts as an ion exchanger even upto pH = 0. The ion exchange effect on a paper may be defined with the help of Ri which is equal to the Rf value on untreated papers ($R_{fu}$) - the Rf values on treated papers ($R_{ft}$) only in about 4N nitric acid the exchanger become unionized and Ri = 0. As the pH increases the Ri also increases till at pH = 3, the Ri is maximum. Therefore at this pH the ion exchange effect is maximum. Another important conclusion can be obtained by comparing the plots for K, Ca and Ga. If we consider the change in Rf values from pH = 0 to pH = 2 than it is apparent that this change is in the order Al > Ca > K, which is to be expected considering the increase in charge on these ions.

The ions Sm, Nb, Nd, Pr, Ti, Ag, Se, In, As, Bi, Tl, and Pb show similar behaviour. They are all strongly adsorbed by the paper and they have very low Rf values. Au, Pt and Hg show an

exceptional behaviour. In this case Ni is either zero or it is very small. These ions are probably negatively charged as in the case of Au and Pt or they are mostly uncharged as in the case of Hg.

The results given in Table XIX shows that the sequence of Kd values differs from that which is predicted from the Rf values. If we consider that the sequence of elution can be predicted from Kd values it follows that the Rf values are not reliable for the prediction. The reasons for this discrepancy are as follows:

1. In paper chromatography the solvent ascent is so fast that there is no time for achieving equilibrium.

2. There are some ions which definetely interact with the paper in a way different from the ion exchange material.

3. The material deposited on the paper has a different composition from that obtained by actual precipitation in a vessel, and since the Kd values depend upon the composition of the material. Therefore they are found to be different.

Owing to the facts mentioned above it is difficult to agree with Alberti that the elution sequence can be predicted by Rf values. At best the Rf values are only a rough guide and that too when they differ from one another considerably.

TABLE - XIX

A comparison of Kd values and Rf values of some metal ions on stannic antimonate.

| Solvent system / Values | Kd values | Rf values |
|---|---|---|
| 1M $HNO_3$ | Mg = Ca > Sr > Ba | Sr > Mg = Ba > Ca |
| | Zn > Hg > Cd | Zn > Cd = Hg |
| .01M | Ca > Mg > Sr > Ba | Sr > Mg > Ba > Ca |
| | Zn > Hg > Cd | Cd > Zn > Hg |

The separations developed here are only symbolic in nature. They show the great versatality of the stannic antimonate papers, using only aqueous solutions of nitric acid and a much larger number of separations are possible which can be easily predicted by the plots shown here.

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